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Resistivity Characterization for Carbon Based Conductive Nanocomposite on Polyethylene Terephthalate and Thermoplastic Polyurethane Substrates

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ABSTRACT

Nanotechnology has gained a lot of focus in recent years due to its application in multi-disciplinary fields such as chemistry, electronics energy, and biology. Wearable electronic consists of nanocomposites liquid-solid conductive ink and flexible substrate. This study characterizes the electrical characteristic of the conductive ink with unloaded condition. The conductive ink was printed with four patterns; straight, curve, square and zig-zag patterns. Sheet and bulk resistivity results indicated the decrement of resistivity of all four patterns with the increase of the conductive ink width. From the result, it showed that the resistivity inside the conductive ink increased such as constriction resistance, tunnelling resistance and the number of squares of the meandering trace as compared to similar lengths of a straight-line trace. Size of the particle also affected the contact area and electrical flow between the conductive ink particles. Meanwhile, individual results for each pattern had its own function inside the circuit track.

Keywords: Liquid-Solid Conductive Ink, Polyethylene Terephthalate, Stencil Printing Method, Wearable Electronics.

1. INTRODUCTION

Nanotechnology has gained a lot of focus in recent years due to its application in multi-disciplinary fields such as chemistry, electronics energy, and biology. Thin film electronics is nanotechnology that is produced with the aim to reduce the physical size and production cost as well as to increase the reliability and improve the performance of the electronic device. Transistor, flexible displays, radio-frequency identification (RFID) tags, touch screens, solar panels microcontroller and micro-electronic are examples of the applications of flexible electronics [1-4]. Thin film usually uses nanocomposite conductive ink as the medium with flexible and stretchable substrate [5-6].

Conductive ink is an insulating polymer matrix that is transformed into conductor [7-10]. The conductive filler is loaded into the composite polymer until it reaches the percolation threshold, which is the result of continuous linkages of the filler particles. Merilampi produced silver conductive ink patterns with sheet resistance that varied between 0.04 Ω/sq and 0.13 Ω/sq [11]. Insulated composite polymers are usually grouped into thermosetting resins and

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thermoplastic resins, where the former is three-dimensional, which cannot be melted after being heated repeatedly. Whereas, the latter are chain polymers, which can melt again after being heated or even after being molded.

Meanwhile, the conductive filler is usually metallic-based, and carbon based. This conductive filler material has good conductivity and low resistivity, but conductive filled composites have a resistance with the value of several magnitudes higher than their pure condition.

The sheet resistivity and bulk resistivity of conductive ink are studied in order to characterize the electrical properties of the conductive ink. Resistivity is a fundamental characteristic of electrical materials. Resistors impede current flow, causing a voltage drop when placed in an electrical circuit. The unit for resistance is Ohms (Ω), which is defined as the amount of resistance required to create a voltage drop of 1 volt (V), when the current flow is 1 Ampere (A). Ohm's law theory states that the resistance of a material is the applied voltage divided by the current drawn across materials between the two electrodes. Metallic conductive ink has low resistivity due to its metal behavior but composite conductive ink has higher resistivity as compared to metallic conductive ink. The two or four points probe method is the most popular technique to measure the resistance due to its capability to minimize the parasitic effects of contact resistance.

The thickness and width of the trace help establish power rating and the number of squares is exploited to determine the device's resistance. As stated by Ruschau, the resistance inside small case size devices can be maximized by increasing the number of squares in the trace design [12]. This shows trace that a meandering pattern has higher resistance as compared to a straight line with a similar length due to the increase in the number of squares. Besides that, the percolation linkage for every particle should be considered as a series of resistors. Every particle and every contact on the particles contribute to the total resistance in the traces, which are the constriction resistance and tunneling resistance. A resistance that is related to the constriction of electron flow through a small area when two conductive particles meet, is known as constriction resistance. In another case, Merilampi and Hu recommended that tunneling is a vital electrical transportation phenomenon at the percolation threshold where the filler materials concentration is about 10–30 vol.% [11-15, 17-20].

However, nanocomposites show excellent properties where they have excellent high surface to volume ratio of the nanofiller or high aspect ratio, exceptional strength and toughness, good electrical and thermal conductivity with low cost and the ease of processability [7]. Electrical conductivity that can fulfill the needs of the application and mechanical properties of the ink is important [11]. So the ink must be free of defects such as pore, delamination, porosity and crack, and must have good adhesion between substrate and ink [9-11].

In this paper, four patterns of conductive ink were printed on polyethylene terephthalate (PET) and thermoplastic polyurethane (TPU) substrates with three different trace widths such as 1 mm, 2 mm, and 3 mm. These patterns were commonly used inside a circuit trace. After that, the samples were tested with several tests such as sheet resistivity, bulk resistivity, and morphology to characterize their electrical characteristics for several parameters under static condition or unloaded condition. From the test, the characteristics for each pattern and the effect of the parameter can be observed and analyzed.

2. MATERIAL AND METHODS

2.1 Sample Preparation

Stencil printing method was used as the printing method to print the samples. Stencil printing method requires the conductive ink to be direct-write on top of the stencil to acquire the desired shape. Carbon black conductive ink was used in this study and cured at room temperature for 30 minutes. Four types of test patterns as in Figure 1 were printed on two different substrates, which were PET and TPU.

As in Figure 1, the test pattern 1 was a straight line, meanwhile test patterns 2, 3 and 4 were designed in meandering shapes, which were curves, squares, and zigzags. All test patterns were designed to be 90 mm in length, 1 mm in thickness, 1 mm, 2 mm, and 3 mm in width, and 20 mm of meandering width. These test patterns were chosen by considering many shapes and edges inside an electronic circuit track.

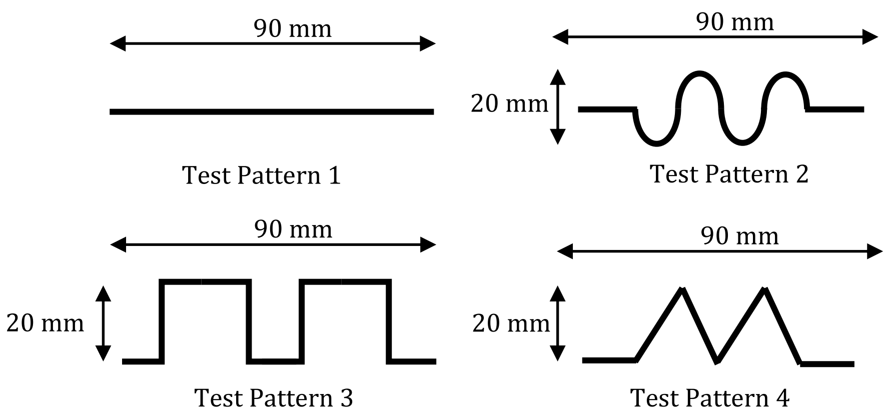


Figure 1 . Conductive ink test pattern.

The PET was used as ink substrate due to its flexibility, good chemical resistance except to alkalis and good mechanical properties such as stiffness, minimum water absorption, strong but inexpensive and thin thickness [12]. Also, the crystallinity of the PET varies from amorphous to fairly-high crystalline. Besides that, TPU which originated from one class of thermoplastic elastomer (TPE) was also used as the substrate for the test pattern.

TPU can be processed into a molten state while recovering rubber-state properties during solidification. TPE is a co-polymeric material that is made from a hard and soft polymeric chain component.

Four test patterns that had been printed underwent a few characterization tests to characterize their mechanical and electrical characteristics such as surface morphology, surface roughness, bulk resistivity, and sheet resistivity. In order to determine the testing points and to ensure the consistency of the data, all the samples were marked at three points as shown in Figure 2 and all the tests were done on the marked points. All the test parameters were summarized as in Table 1.

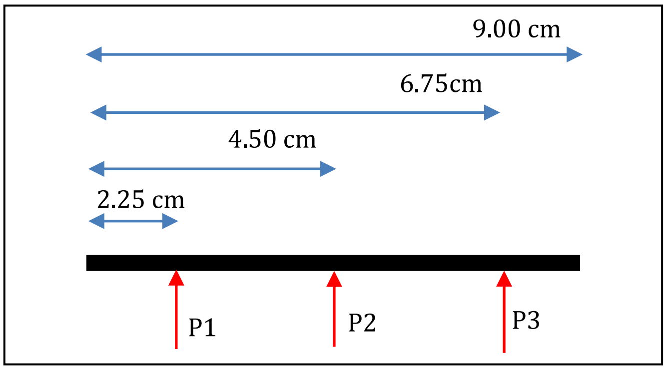


Figure 2. Measurement points on the sample.

Table 1 The summary of design parameter

	Design parameter
Trace patterns	Straight, Curve, Square, Zigzag
Thickness, *t* (mm)	1
Length, *l* (mm)	90
Width, *w* (mm)	1, 2,3
Substrate	Polyethylene terephthalate (PET)
Paste	Carbon Black
Printing method	Stencil printing

2.2 Measurements

Electrical characteristics of the samples such as bulk resistivity and sheet resistivity were observed and measured using 3D non-contact profilometer, multimeter and the four-point probe. All these tests were performed on the samples with the unloaded condition.

2.2.1 Bulk Resistivity

Bulk resistivity was measured by using digital multimeter at four points, which were P1, P2, P3, and P4. The positions from P1 until P3 are as illustrated in Figure 2 and P4 is of ink from end-to-end. Most digital multimeters can perform measurements as low as 0.1Ω and some can measure as high as 300MΩ. Firstly, the negative probe was placed at the start of the conductive ink track and the positive probe was placed on four marked points starting from P1 until P4. This test was done to measure the bulk resistivity that flows along the ink track for each marked distance. The track or circuit must be powered off when measuring the resistivity or with the absence of voltage in order to avoid damages to the circuit.

From this test, the changes in resistance for straight lines, turns or edges for each pattern can be observed. Bulk resistivity value that was obtained from the multimeter showed live reading, which required to be collected manually. All these tests were conducted with three repetitions

2.2.2 Sheet Resistivity

Sheet resistivity was performed using the four point probe machine due to its independence of the square and fairly low resistivity of the thin film [11]. All the samples were measured on marked points as in Figure 2. Firstly, before starting with the measuring process, calibration was done by using a referenced sample of an indium-tin-oxide (ITO) coated glass to ensure the device was functioning well and accurately. The referenced sample was put on the device base under the probe pin, which had four probes and the height of probe pin was lowered until it touched the referenced sample. All the four probes had to be parallel and touched the referenced sample because the current, I flows through the outer probes and induces a voltage, V in the inner voltage probes. Sheet resistivity can also be defined with a mathematical expression as shown in Equation (1).

$$\rho = 2\pi s \frac{V}{I} \tag{1}$$

When all the probes touched the referenced sample, they started to take live readings of the sample. Due to live measurements, RC (resistance-capacitance) a delay was needed as the current inside the sample needed some time to flow up or down to reach the saturation value.

In order to measure the experimental samples, all calibration steps needed to be repeated. Before that, the probe pin height needed to be adjusted again to gain a suitable height for the experimental samples because the PET substrate and the referenced sample had different thickness. When the value was obtained, the enter button was pushed to record the measured value. Lastly, the collected data was imported into the software. All tests were conducted with three repetitions.

3. RESULTS AND DISCUSSION

3.1 Bulk Resistivity of the Test Samples

The total conductivity of polymer composite is controlled with a few different mechanisms and it is a complicated phenomenon. The total conductivity is controlled with a function of conductive filler materials, surface resistance of the filler, conductivity of polymer matrix and hopping conductivity. However, when compared to the conductivity of filler materials, the conductivity of the polymer matrix is small, and it can be neglected. The conductivity and resistivity of the polymer composite had been reported by Merilampi and Mohammed [11-16]. The 3D conductive bond is formed by conductive particles that agglomerate together.

Figure 3 shows the bulk resistivity of printed conductive ink on PET and TPU substrates with three different trace widths that are 1, 2 and 3-mm. Bulk resistivity is used to measure the resistance flow along the conductive ink. All the samples show the same pattern, where the bulk resistivity decreases as the trace width increases. As the trace width increases, the pathway of electron increases. Carbon black primarily has a particle size of 30 to 50 mm and is an excellent material for producing electrically conductive composites. Its particle size leads to significant levels of particle aggregation, which form a large network at relatively low concentration. With the increase in trace width, the amount of ink also increases and forms more network inside the ink.

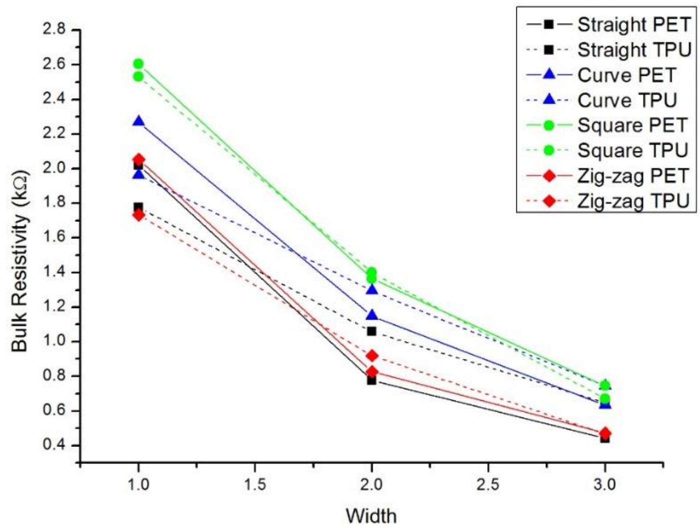
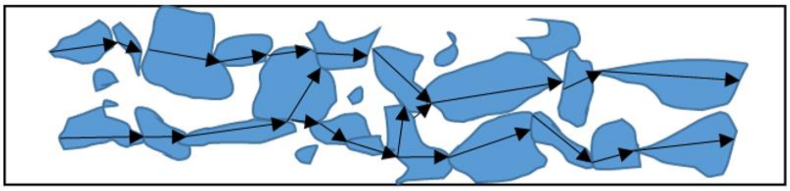
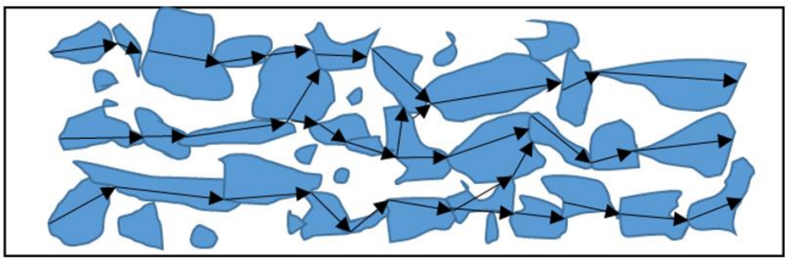


Figure 3. Bulk resistivity for test patterns with PET and TPU substrates.

Based on Figure 3, the ink traces with 1mm width of PET substrate have higher bulk resistivity than ink traces on the TPU substrate for all four patterns. Meanwhile, for ink traces with 2mm and 3mm width, ink traces on the TPU substrate have higher bulk resistivity than ink traces on PET substrate. Conductive ink on the TPU substrate has lower bulk resistivity due to substrate stretchable and its soft nature as compared to PET substrate, which is more rigid. This happens during the curing process when the ink tends to shrink and pull the substrate to crumple closer. This also increases the contact surface between the particles and reduces the particle gap. In addition, the square pattern on the PET and TPU substrates have higher bulk resistivity, which are 2.61 kΩ and 2.53 kΩ for the 1 mm width, 0.75 kΩ and 0.67 kΩ for the 3 mm width. Straight patterns on the PET and the TPU substrates have the lowest bulk resistivity, which are 2.02 kΩ and 1.78 kΩ for the 1 mm width, 0.44 kΩ and 0.65 kΩ for the 3 mm width. Thicker and wider squares usually increase the ability to carry more current and handle more power.



(a)



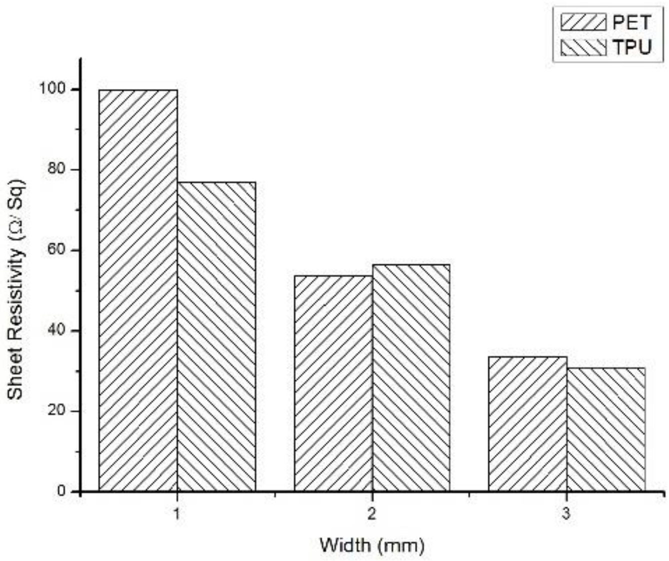
(b)

Figure 4. Particle distribution of the electron flow.
(a) small trace width and (b) wider trace width

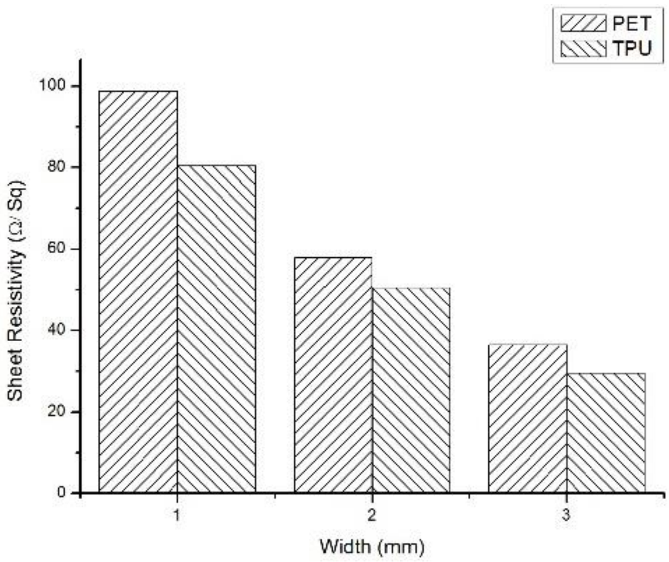
3.2 Sheet Resistivity of the Test Samples

Sheet resistivity is a common electrical property used to characterize thin film and semiconductor materials. Sheet resistance is very useful for chip designers because it simplifies the resistance of the resistor design. Venkel Ltd had studied sheet resistance in serpentine patterns of interconnected squares, which maximized the resistance inside the small case size [1]. The use of serpentine pattern was able to double the resistance in a similar lineal distance.

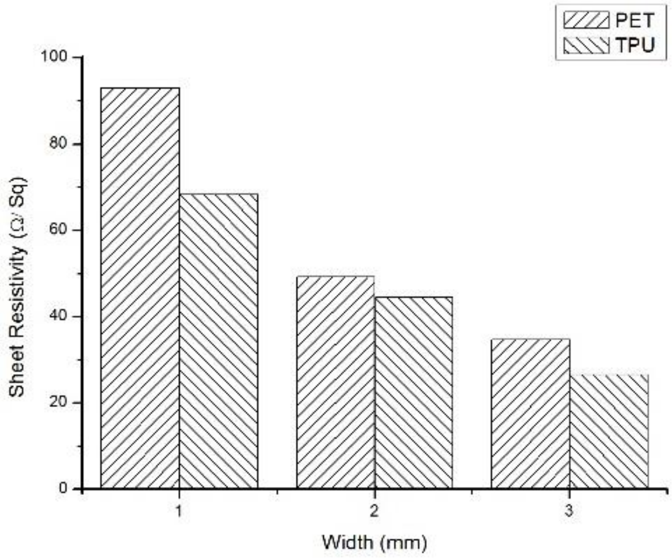
Figure 5 shows sheet resistivity for four patterns on the PET and TPU substrates and all the samples also show a decrease in sheet resistivity as the trace width increases. Sheet resistivity of conductive ink on the TPU substrate is lower than conductive ink on the PET substrate due to its soft surface. So, the carbon black particles come closer to each other and more conductive paths occur for the electrons to move from particle to particle. Sheet resistivity of the conductive ink decreases as the trace width becomes wider because of the concentration of conductive filler that increases with the wider trace. The conductive filler generates electrical contact between the particles and enhances the conductivity of conductive ink as the concentration of conductive filler increases. Merilampi states that the increase in conductive filler concentration increased the conductivity because the increase in filler contact increased the charge carriers [15]. However, the contact area between particles can increase the constriction resistance on the asperities contact.



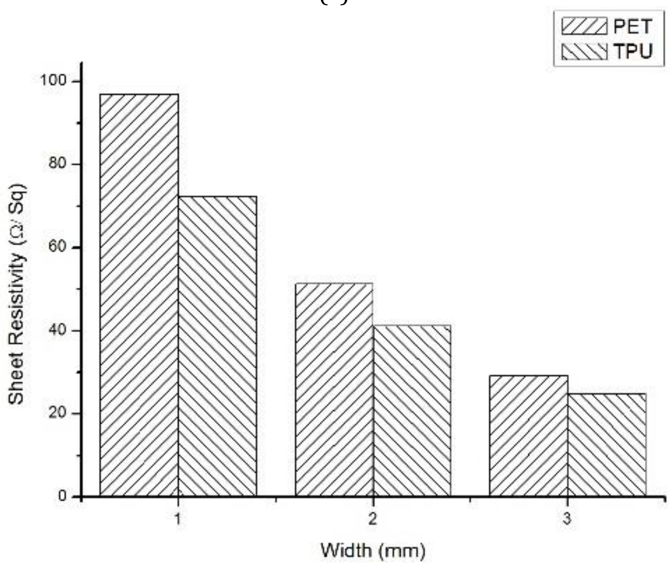
(a)



(b)



(c)



(d)

Figure 5 . Histogram of sheet resistivity comparison for PET and TPU substrates.
(a) straight pattern, (b) curve pattern, (c) square pattern and (d) zig-zag pattern.

In microscopy, the contact boundary surface between two conducting structures is far smaller than the apparent contact area where every surface has peaks and valleys as in Figure 6. The electrical and electron flow near the asperities affect the constriction resistance inside the conductive ink. The smaller the contact area between two peaks, the higher the density of the current flow in the contact area. This shows that conductive ink with 1 mm width has less contact spots as compared to the 2 mm and 3 mm widths.

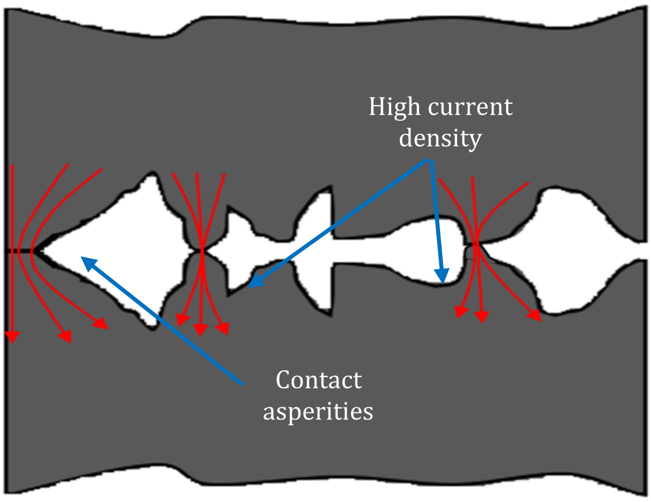


Figure 6 . Diagram of constriction resistance.

3.3 Scanning Electron Microscope Analysis

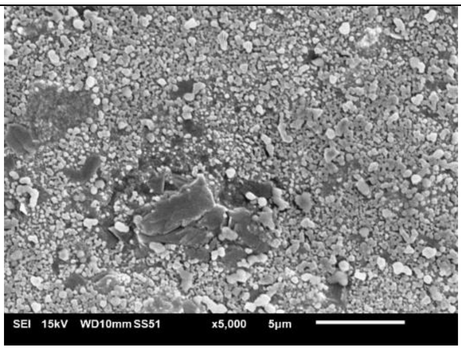
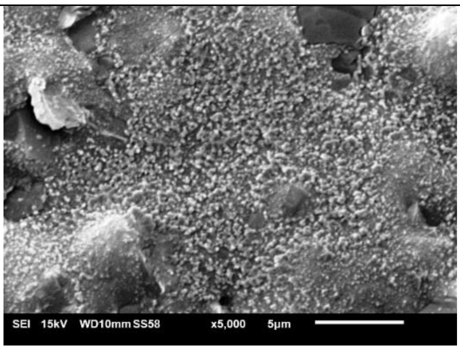
Table 2 shows the particle size of conductive ink for the three widths. The cross-section images were taken by using scanning electron microscope (SEM). It shows that the particle size of conductive ink on the PET substrate is about 0.47 µm to 0.62 µm and the size of conductive ink on the TPU is about 0.22 µm to 0.51 µm.

In addition, Table 3 shows the SEM cross-section images for 1 mm, 2 mm, and 3 mm traces width for the PET substrate and TPU substrate, respectively. As for the images of the 1 mm width, they show the carbon black particles with the gap for most of the particles. Images for the 2 mm width show that many particles have merged together and the images for the 3 mm width show that more particles have merged together.

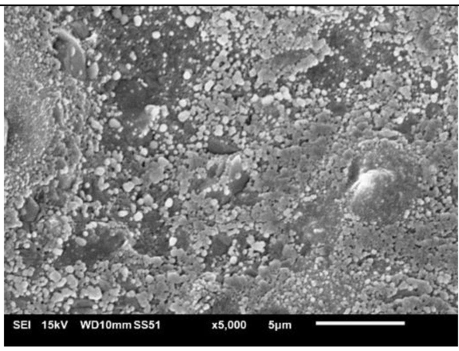
Table 2 Particle size of the conductive ink

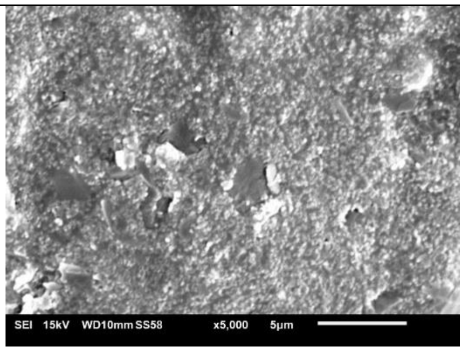
	PET				TPU			
	Average (µm)	**Min (µm)**	**Max (µm)**	**Standard deviation**	**Average (µm)**	**Min (µm)**	**Max (µm)**	**Standard deviation**
1mm	0.623	0.244	1.549	0.388	0.512	0.161	1.122	0.266
2mm	0.511	0.201	1.006	0.235	0.225	0.063	0.419	0.100
3mm	0.473	0.165	0.960	0.230	0.236	0.133	0.558	0.109

Table 3 SEM images for conductive ink trace width with 1 mm, 2 mm and 3 mm

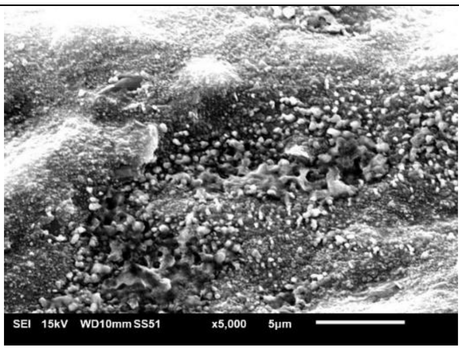
Substrates	PET	TPU
1 mm		

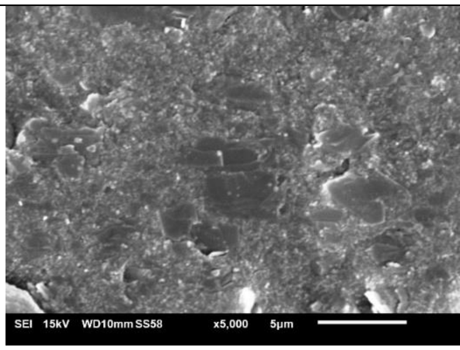
2 mm





3 mm





4. CONCLUSION

Carbon black is one of the carbon-based materials that has been used in conductive ink. It is cheap and easy to mass produce because it can be quite easily obtained. In this study, the stencil printing method was used to make the test samples with several varying parameters such as various patterns, widths, and substrates. All test samples were characterized in the static condition to determine their bulk resistivity, sheet resistivity, and morphology. The sheet resistivity and bulk resistivity were measured with the four-point probe and multimeter. These two results had the same condition, where the resistivity decreased with the increase in the track width. For both substrates, the zig-zag pattern had the highest sheet resistivity and the straight pattern had the lowest sheet resistivity. Meanwhile, for all the three track widths, the straight pattern had the lowest bulk resistivity and the square pattern had the highest bulk resistivity. There are some factors involved that make the resistivity inside the conductive ink increase such as, the constriction resistance, tunneling resistance and the number of squares of the meandering trace as compared to a similar length of a straight line trace. The size of the particle also affects the contact area and the electrical flow between the conductive ink particles.

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