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The Behaviour of Graphene Nanoplatelates Thin Film for High Cyclic Fatigue

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ABSTRACT

Conductive inks thin film is a composite with conductive material that can replace a conventional and rigid electronic device into one that is flexible and thin electronic device. The thin film behavior was investigated in condition when it was subjected to cyclic bending up to 5000 cycles. The goal of this study is to obtain data for developing electrical packaging with different patterns. Surface roughness, sheet resistivity and bulk resistivity of thin films were measured at every thousand bending cycle. The surface roughness decreased as the cycles increased, meanwhile the sheet and bulk resistivity increased as the cycles increased. This GnP thin film could endure high cycle stress up to 3000 cycles before it failed.

Keywords: Conductive Ink, Graphene, Cyclic, Fatigue, Bending, Thin Film.

1. INTRODUCTION

Electronic devices and semiconductor fields are being developed to become more high-end and complex, but they are mostly still rigid and inflexible. Researchers have studied a new system of electronic devices that is flexible, transparent and can be incorporated between electronic devices and semiconductor component to produce novel devices such as e-textiles, embedded electronics, wireless sensors, foldable display panel and transparent photodetector [1-3]. In the case of flexible and wearable devices, they must be able to sustain their function even when subjected with certain conditions such as bend, twist and vibration. Conductive ink thin film possesses the ability to fulfill these requirements which cannot be achieved by conventional electronic. Conductive ink is a conductive polymer composite, which the insulating polymer is mixed with nanoparticle conductive filler until it reaches the percolation threshold due to continuous linkages of filler particles. Epoxy resin is one of the most versatile polymer and it can be grouped into thermosetting resin and thermoplastic resin.

Moreover, epoxy resin can be molded to any desired shape based on the final product requirements and needs, and it can be cured by applying the heat. In other cases, conductive filler needs to have the ability to conduct the electricity and has low resistivity. But, conductive filled composite has larger resistance as compared to its pure condition [3]. Maizura produced conductive ink thin film with silver as filler base with the sheet resistance in the range between

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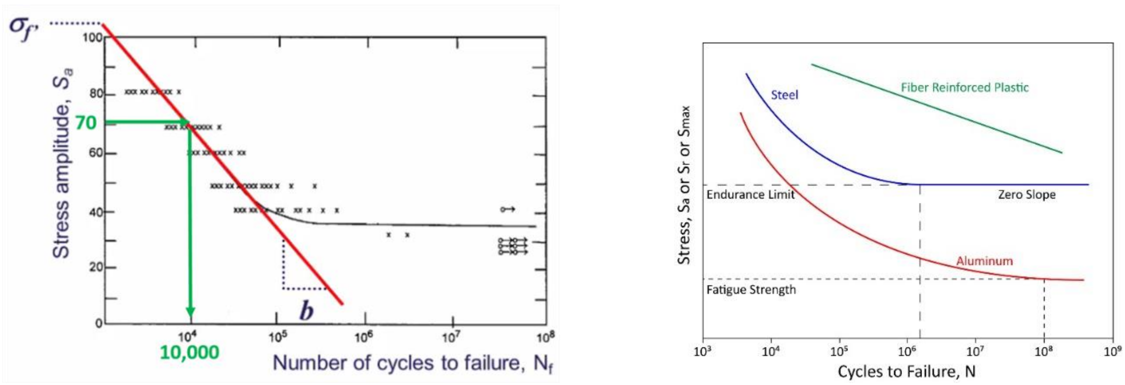
0.04 Ω/sq to 0.13 Ω/sq and produced graphene composite thin film, which had sheet resistance between 4 MΩ/sq to 6 MΩ/sq [4].

The usage of epoxy resin and their curing application are also important factors contributing to thin film mechanical properties other than the flexible substrate. Flexible and wearable electronic devices must be able to withstand the dynamic loading to a certain degree. The atoms of solid shift from their equilibrium state under loading and in order to restore to the initial shape, the restoring force is induced to oppose the deformation from occurring [4]. This phenomenon shows the process of mechanical behavior of solid in response to the mechanical stress. The formation of defect and propagation appear in order to relief the mechanical stress as the load increases. Shin had studied the effect of low cyclic loading and bending deformation on GdBCO coated conductor (CC) tape, which has good strain tolerance to bending deformation [5]. In this study, they applied several mode of cyclic loading such as axial, transverse and bending to the samples. Due to the cyclic mode of each loading configuration, the superconducting characteristics of CC tapes degrade at an early stage. Damages such as micro-crack, delamination occurred on interface among layers within the CC tape after 100 cycles.

Cyclic fatigue test is used to measure the applied stresses in axial, flexural or torsional of material to determine the failure after lengthy periods of repeated stress or strain. In the S-N curve where stress versus the logarithm of the number N of cycles to failure, it shows the smaller number of cycles that the material is able to sustain before failure when the magnitude of stress increases [6-11]. The S-N curve in Figure 1(a) becomes horizontal at the higher N values for some ferrous and titanium alloys, which is called fatigue limit or endurance limit. In another case as in Figure 1(b), most nonferrous alloys do not have fatigue limit and the S-N curve keeps decreasing as the N values increase. Due to this pattern, the fatigue can absolutely occur at any magnitude of the stress. This phenomenon can be specified as fatigue strength that indicates the stress level at which the failure will occur for certain number of cycles [6,7,12].



(a) (b)

Figure 1 . Stress amplitude (S) versus logarithm of the number of cycles fatigue failure (N). [6-7] (a) a material that displays a fatigue limit and (b) a material that does not display a fatigue limit.

In this paper, graphene nanoplatelates composites were mixed and printed on polyethylene terephthalate (PET) substrate with four different patterns. These samples were tested with cyclic bending up to 5000 cycles and characterized electrically and mechanically. This test is able to demonstrate the graphene composite thin films behavior before and after the cyclic stress was applied onto them.

2. MATERIAL AND METHODS

Graphene Nanoplatelates (GnP) were purchased from Sigma Aldrich and used as filler for this study. The GnP used has particle diameter less than 2 microns, surface area of 500 m^2/g and

12.01 g/mol of molecular mass. Bisphenol-A diglycidyl (DGEBA) ethers, that is made up of epichlorohydrin and bisphenol-A was used as the polymer binder. This colorless resin from Sigma Aldrich with the trade name of Araldite 506 epoxy resin is the thermosetting polymer group with the density of 1.168 g/ml and viscosity value between 500 – 750 mPa.s at 25 ºC.

In addition, The Hunstman polyetheramine D230 hardener was used as hardener to complete the curing process. This amine group curing agent has the density of 0.947 g/ml and viscosity of 9 mPa.s at 25 ºC.

2.1 The GnP Nanoplatelates Inks Preparation on Flexible Substrate

Conductive ink was produced when mixing the conductive filler and binder together in a 0.35: 0.65 volume ratio. The GnP nanoplatelates were used as the filler and the combination of epoxy resin and hardener as binder. 20% of the hardener from epoxy resin volume was used as hardening component. The amount of hardener can affect the properties of cured resin, with which the hardness value improves when the amount of hardener increases [13]. However, its content limits the fraction of resin available for the cross linking and produces a rigid and stiff interface. This means that 20% of the hardener content is the most suitable hardener amount in conducting the cyclic bending test because excessive amount can cause the conductive ink to break upon bending. The filler/binder is then mixed using centrifugal mixing machine at 2000 rpm for 10 minutes.

To fabricate the thin film, PET substrate with 150 mm x 40 mm of length and width is prepared. After that, the printing is done via direct stencil print method with four different patterns as in Figure 2.

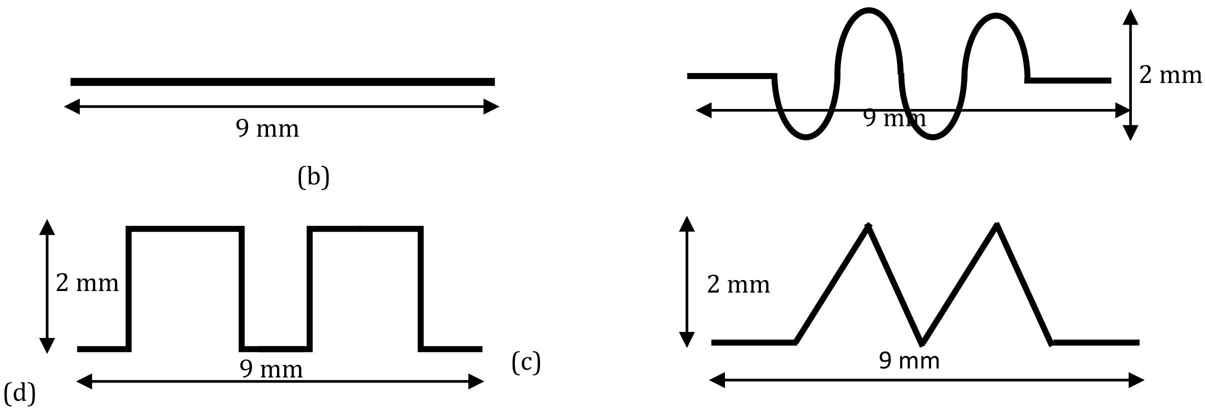


Figure 2. Conductive ink pattern design with a width and thickness of 3mm and 1mm. (a) straight line pattern, (b) curve pattern, (c) square pattern and (d) zig-zag pattern.

The thin film is cured inside an oven with the temperature of 100 ºC for 30 minutes. During the curing process, the conductive ink that is in a viscous liquid state changes into a hard and solid state. At the same time, during this process, several complex chemical and physical changes occur inside the conductive ink, which lead to cross-linking network. Table 1 summarizes the parameters of conductive ink thin film fabrication.

Table 1 The inks, print methods, substrates, test patterns, and curing parameters for experiments performed in this study

Filler Material	Print Method	Substrate	Test Pattern	Curing Parameter
Graphene nanoplatelates	Stencil direct print	Polyethylene Terephthalate (PET)	Straight line, curve, square and zig-zag	100 ºC, 30 min

2.2 Cyclic Bending Experiment and Measurement

Dynamic loading in cyclic bending form was applied on each sample to study the thin film condition. The samples were bent up to 5000 cycles by using bending test rig as in Figure 3 and measured after every 1000 cycles. The sample was clamped at both ends with one side being fixed and other side could freely move. The test rig was powered by a power supply source and the sample was bent by compression movement until the bending section was parallel to each other.

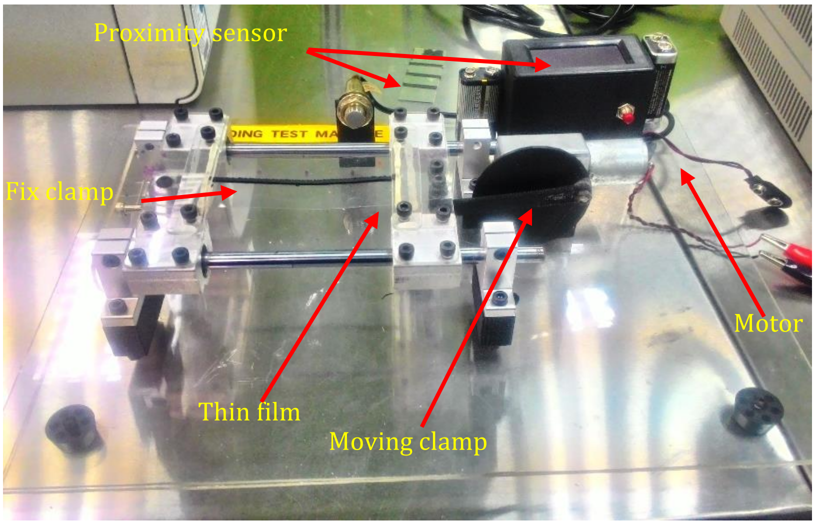


Figure 3 . Cyclic bending test rig setup.

Resistivity is a resistance of a given material to electrical conduction. Although the flow of the electric current is resisted by the materials, a few materials are better in conducting the current than the others. It enables the way of comparing different materials in resisting or allowing the current to flow. Furthermore, resistivity can be referred to some specific resistance such as sheet resistivity and bulk resistivity. Sheet resistivity is usually measured using four-point probe device such as the surface resistance of the thin film, which is fairly of small value of resistivity [4]. The four-point probe uses four-point terminal, which the voltage source supply supplied separates the voltage to eliminate unnecessary resistance inside the system. In this experiment, the sample was placed under the probe pin after the initial set-up procedure when the pin was lowered to begin the measurement. Moreover, the sample was measured at three fixed points to ensure the value uniformity for all samples.

For bulk resistivity, the sample was measured using digital multi-meter. Bulk resistivity uses a two-point terminal, where the difference in sheet resistivity measures resistance through the thin film length. For this method, the negative terminal was placed at the end of the film and the positive terminal pointed to the points that had been marked. All the measurements were repeated three times to get the average value.

3. RESULTS AND DISCUSSION

3.1 Surface Roughness of Thin Film

The surface roughness, Ra, of the ink film are shown in Table 2. The surface roughness can provide a general idea or understanding about the amplitude of wavy surface. To maintain the uniformity and a similar ink surface condition and roughness, the conductive ink paste was printed in one direction with constant speed while the other factors such as printing force and pressure were neglected. From the same table, all patterns show a declining order in ink surface roughness value and they become smoother as the bending cycles increase.

Table 2 Surface roughness data of four patterns when subjected to cyclic bending from 0 cycle until 5000 cycles

Bending Cycle	Surface Roughness, Ra (μm)			
	Straight	**Curve**	**Square**	**Zig-zag**
0	1.69	2.19	1.89	1.88
1000	1.60	2.69	1.92	1.81
2000	1.94	2.09	1.76	2.17
3000	1.70	2.30	1.87	1.54
4000	1.01	1.22	1.29	1.34
5000	1.48	2.15	1.73	1.34

When the thin film was subjected to compression bending cycle, the ink surface was under tensile condition as stated in Euler and Bernoulli beam theories and causing the surface to expand and become smoother in micron scale. Crack formation as shown in Figure 4 was due to the stresses on the surface. The theory was used to describe the strength of beams under bending. The stresses in the film were caused by both bending movement and shear force. The stress due to latter factor was maximum along the neutral axis of the film because there is no situation in reality in which the pure bending happens. Furthermore, the maximum tensile stress that occurred at the top and the bottom surfaces were compressive stress. In Euler and Bernoulli beam theories, there are some assumptions that have been made such as the deformation occurrences that are small and linear isotropic and the Poisson ratio are neglected.

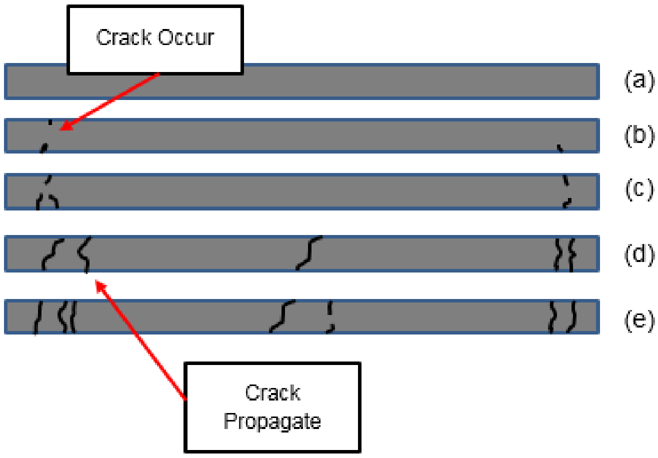


Figure 4. Formation of crack nucleation, crack propagation on thin film after every thousand cyclic bending.
(a) first, (b) second, (c) third, (d) fourth and (3) final cracking.

When the thin film is under cyclic fatigue, crack formation can occur, and the same figure shows the bending crack formation at the end of the thin film after 2000 cycles. Then as the cycle increased, the crack had propagated and combined from each side to form a full propagated crack across the ink width. Repeated bending on the thin film causes stress concentration to occur at the top surface. Fatigue crack usually starts as stress is concentrated and then propagates when the concentrated stress exceeds the material's theoretical cohesive strength. The theory of bending is then illustrated by Figure 5.

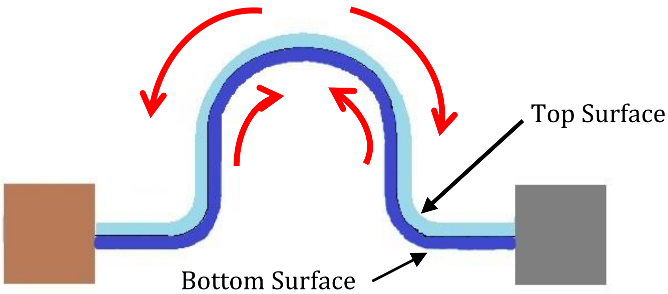


Figure 5. Compression bending method that causes two stresses to occur on the top surface (tensile) and the bottom surface (compress).

3.2 Bulk Resistivity and Sheet Resistivity of Thin Film

Figure 6 and Figure 7 show the increase of bulk and sheet resistivity as the bending cycle increases for all four patterns. With continuous bending, the bended film surface had been subjected with maximum tensile stress, so the film width and microstructure may had changed. The width of film stretched and increased the filler inter particles distance. When this, happens the constriction resistance increases because the contact asperities between the particles surface have reduced. Other than that, tunneling resistance will also increase and eliminate the electrical conductivity threshold. Tunneling resistance is a phenomenon where it allows the current flow between untouched particles or the two particles coated with any insulating film, creates certain gaps such as the oxidation process on the particles surface [3]. Many researchers have suggested that the filler concentration to be between 10-30 vol.% to achieve percolation threshold [6,10]. Between this filler concentration, the particles have enough distance to form the tunneling effect [8-9]. The crack nucleation causes the inter filler to separate and leads to partial breaking of the 3D network. It increases the resistance in proportion to the increase of bending cycles and also creates another crack nucleus. As the bending cycle increases, the crack starts to grow and propagates bigger delamination and increases the resistance between the particles as for bulk resistivity and sheet resistivity values. The 3000 to 5000 cycles show huge increment of resistivity.

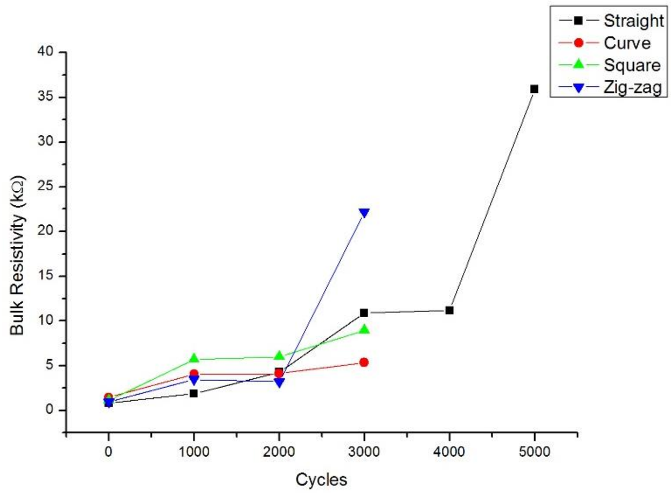


Figure 6. Graph of bulk resistivity over the period of bending cycles.

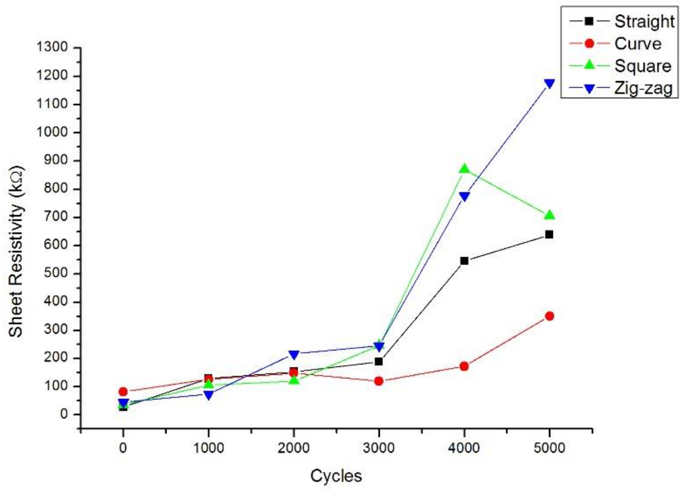
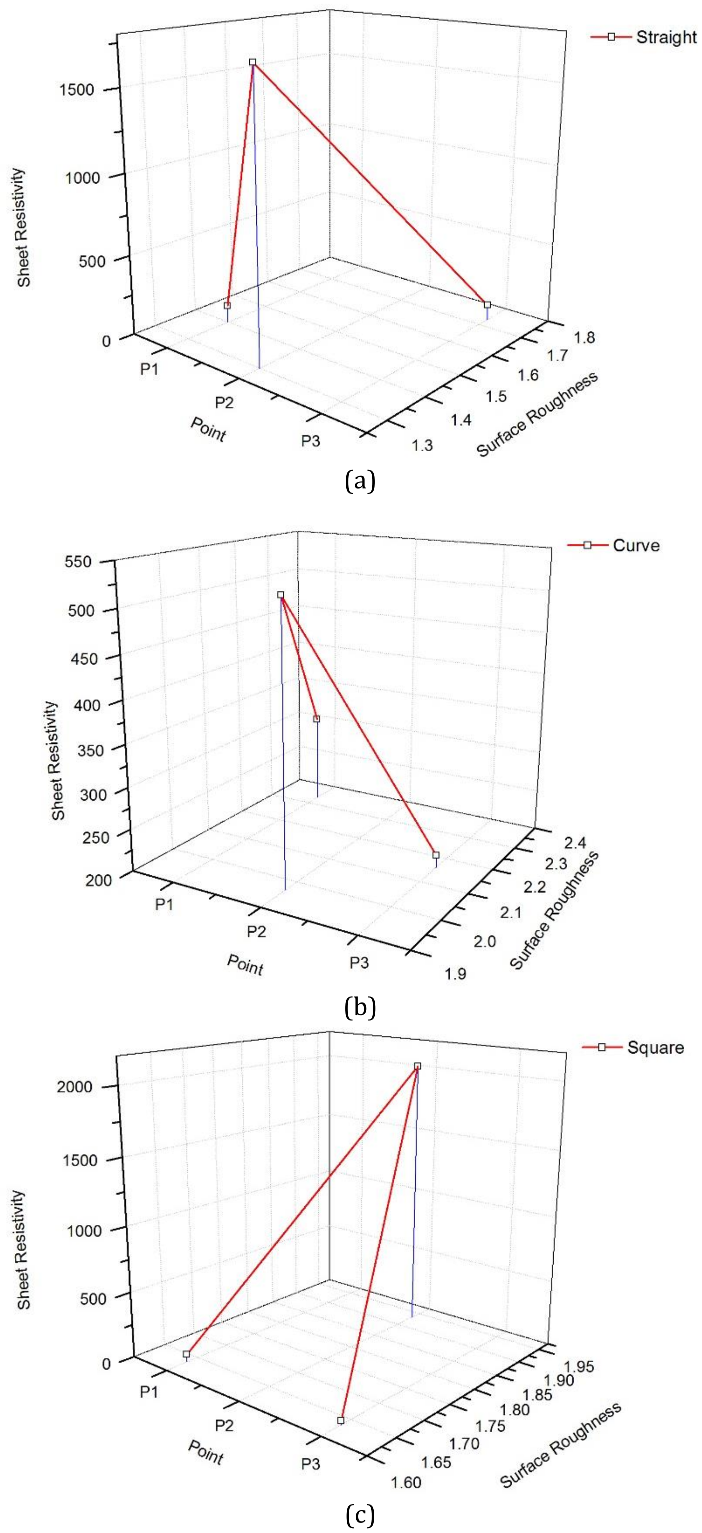
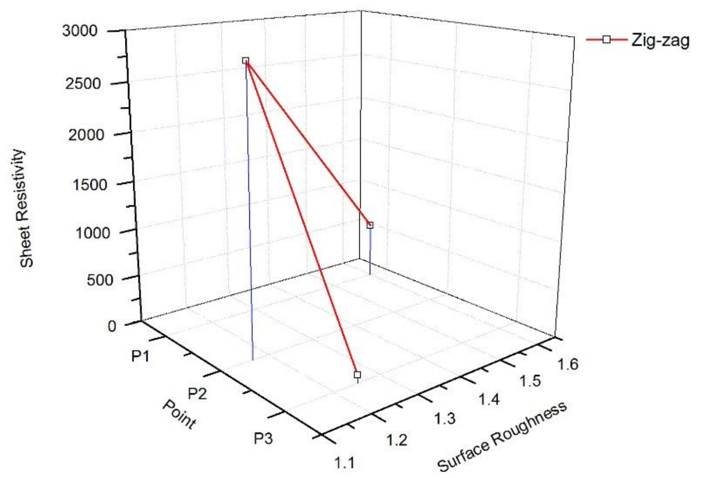


Figure 7. Graph of sheet resistivity over the period of bending cycles.

In addition, surface roughness also affects the sheet resistivity and bulk resistivity of thin film. When the microstructure inside thin film changes, the surface roughness also changes as mentioned previously. Figure 8 shows a graph of sheet resistivity over surface roughness and the point measured for thin film at 5000 cyclic bending. The sheet resistivity at P2 is higher where the surface roughness is the lowest except for the square meandering pattern.


Straight
Sheet Resistivity
0
500
1000
1500
Point
P1
P2
P3
Surface Roughness
1.3
1.4
1.5
1.6
1.7
1.8
(a)
Curve
Sheet Resistivity
200
250
300
350
400
450
500
550
Point
P1
P2
P3
Surface Roughness
1.9
2.0
2.1
2.2
2.3
2.4
(b)
Square
Sheet Resistivity
0
500
1000
1500
2000
Point
P1
P2
P3
Surface Roughness
1.60
1.65
1.70
1.75
1.80
1.85
1.90
1.95
(c)



(d)

Figure 8. Graph of sheet resistivity over surface roughness and the point measured for thin film at 5000 cyclic bending.
(a) Straight, (b) curve, (c) square and (d) zig-zag.

4. CONCLUSION

Graphene nanoplatelate is one of the carbon-based materials that has been used as the filler material for conductive ink owing to it being an excellent electric conductor, it possesses good mechanical properties and its low-cost production. In this study, stencil printed GnP conductive ink behaviour when subjected to cyclic bending up to 5000 cycle was investigated. During the experiment, the surface roughness of thin film had become smoother as the bending cycles increased. This was due to the Euler-Bernoulli beam theory effect. Other than that, sheet and bulk resistivity also increased as bending cycles increased. During the bending cycle test, the film had stretched, and the filler particles distance had increased, hence increasing the constriction and tunnelling resistance. The resistivity of thin film increment was also because of the formation of crack nucleation and crack propagation. Lastly, the GnP thin film could endure the bending stress up to 3000 cycles before it failed. The behaviour of enduring high cyclic fatigue was quite moderate. Cyclic fatigue usually involves bending, tensile and torsion stresses. With the exception of the cyclic bending, cyclic tensile and torsion can be implemented on the conductive thin film for future studies and further development.

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