

Thermo-Mechanical and Adhesion Performance of Silver-Filled Conductive Polymer Composite (SFCP) Using Thermoplastic Polyurethane (TPU) Substrate

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ABSTRACT

Emerging of conductive metal filler in nanoscale like Silver-Filled Conductive Polymer Composite (SFCP) ink is one of the important technology for electronic interconnects future. Among the key challenges in the successful development of such materials are to offer high electrical conductivity and good adhesion in polymer-based substrates without compromising on the mechanical reliability of such devices. This paper discussed the characteristics of Thermoplastic Polyurethane (TPU) based-materials in terms of their sustainability, wettability and SFCP conductivity of thermal effect (room temperature – 25°C), 40°C, 60°C and 80°C). The experimental work involved electrical conductivity measurement using a Four-Point Probe, contact angle measurement and surface roughness analysis. Surface morphology analysis was carried out by using Axioscope 2MAT Optical Microscope and Scanning Electron Microscopic (SEM). The results show that sheet resistance of SFCP increased with an increasing strain and decrease with the increasing of temperature. The above results were observed due to the crack formation against strain but the presents of temperature cause the silver (Ag) particle to expand, filled the gap and form network path for electrical conduction even at maximum temperature and strain (80°C at 80%). Moreover, the TPU shows low wettability that exhibits poor adhesion between SFCP and TPU substrate due to reducing in the contact area between adhesive and substrate that cause the surface has low surface energy when exposed to variation of temperature.

Keywords: Stretchable Silver Conductive Ink; Thermal; Wettability; Surface Roughness; Sheet Resistance.

1. INTRODUCTION

The wearable technology emerged as one of the most important substrate technology. It is applicable in various applications especially when the flexibility requirements are needed. The wearable substrate performance depends on two main factors that are the adhesion capability of the substrate to hold the interconnect material deposited onto it and also conductive filler materials used reinforce with polymer composite as interconnect material that also known as polymer-based electrically conductive adhesives (ECAs) [1,2]. Based on Ghanem study, the adhesion of the substrate determines the holding capability of the interconnect material during the action of bending and stretching as well as their strength depending on the interaction

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between them [3]. The contact angle is one of the methods which was being used to explain its adhesion is through wetting behaviour of the surface obtained. The wetting surface with high surface energy indicates a small contact angle and its exhibits more adhesion due to a large contact area between the solid surface and substrate and vice versa [4].

In comparison with Sn/Pb solder technology, the use of ECAs as interconnect material in semiconductor electronic industry gives more benefits such as environment-friendly, inexpensive production process, easy manufacturing conditions, and low stress on the substrates [1,5]. The used of metallic conductive filler in ECAs helps to further increase the electrical performance of ECAs. Silver (Ag) is used in this research as a metallic conductive filler in Silver-Filled Conductive Polymer (SFCP) ink that give much more advantages like (i) high electrical conductivity, that is approximately $15.87 \text{ n}\Omega\text{-m}$ whilst the thermal conductivity is 429 Wm-1K-1 of any metal; (ii) easy to process into ideal shapes; and (iii) has significantly higher conductivity of its oxides than those of other metals [6,7].

In this research, the Thermoplastic Polyurethane (TPU) was used as a substrate for SFCP ink and it belongs to polyester polymer group that has both flexible and stretchable properties and may exhibit strain up to 100% [1]. Nonetheless, studies related to TPU substrate properties especially when applied strain and thermal respectively with SFCP deposited is relatively scanty, however, few existing studies reveal that the adhesion performance is degraded due to cracking formation but increased in sheet resistance with the presence of temperature. Instead, to-date, the effects of thermo-strain of SFCP on TPU substrate is still not fully investigated. It is important to fully understand the performance of TPU and SFCP under these conditions in order to expand its functionality to the next level. Therefore, this paper investigates the correlation of the adhesion and bondability between SFCP and TPU which resulted in surface sheet resistance. The effect of strain and temperature including thermal test, strain test, thermo-strain test and wettability test under variation of temperatures were investigated. Morphological study of the SFCP was characterized using Axioscope 2MAT Optical Microscope and Scanning Electron Microscopy (SEM) while Four-Point Probe for resistivity measurement. Wettability test was done by using self-invented contact angle measurement tools.

2. SAMPLE PREPARATION & EXPERIMENTAL SET-UP

2.1 Materials

TPU width of 0.1 mm with a visually translucent polyester film was obtained. Physically, TPU is a flexible and stretchable polymer film. The conductive ink used in this experiment containing micron-sized silver flakes conductive fillers binds with polymer resin.

2.2 Thermal properties of TPU

Thermal properties of TPU was analysed by using DSC Perkin Elmer S4000 to determine suitable heating temperature. A 6.21 mg of TPU was weighed into a TA Tzero standard aluminium pans and was filled into DSC. The data were collected at a rate of heat flow of $10^\circ\text{C}/\text{min}$ over temperature from -40 to 300°C .

2.3 Sample Preparation and Characterization Method

2.3.1 Thermo-Mechanical Test

Three in-situ tests were chosen to analyse the thermal and mechanical (thermo-mechanical) properties of SFCP ink and TPU are the thermal test, strain test and thermal and strain (thermo-strain) test. Figure 1 (a) - 1(c) show the experimental setup for the thermo-mechanical test. The

SFCP was mixed with a solvent and stirred manually for 5 minutes at room temperature. Next, the SFCP was placed on a stencil for ink printing and pulled straight by a squeegee to allow the SFCP to fully cover the TPU. Then, the samples were cured at 80°C for 1 hour. For the thermal test in Figure 1(a), the conductive ink samples were heated using a hot gun at three levels of heat; low level (40°C), intermediate level (60°C) and high level (80°C) for 30 seconds before measuring the sheet resistance by using Four-Point Probe. The sample at room temperature (RT) was used as a benchmark of the testing. The levels of heating were measured in-situ by using thermal imaging analyser.

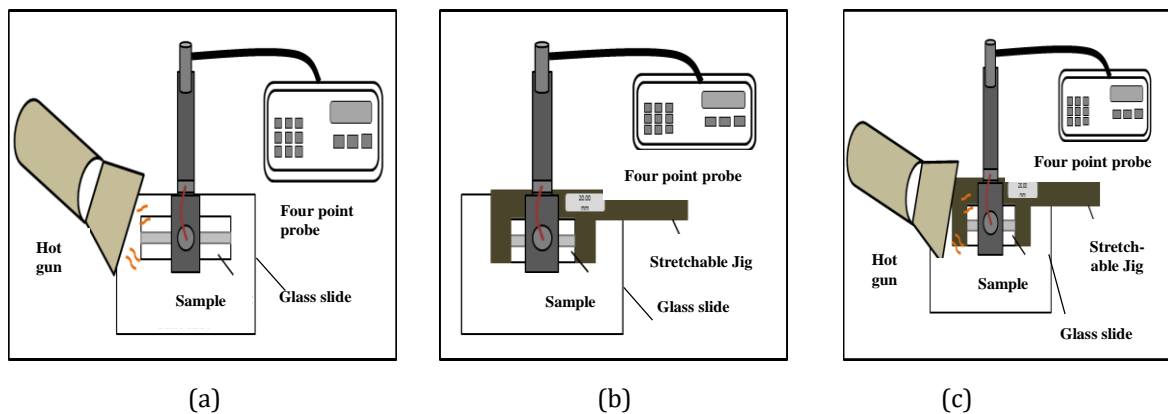


Figure 1. Experimental Set-up for: (a) Thermal test, (b) Strain test, (c) Thermo-strain test.

For the strain test shown in Figure 1(b), the samples were stretched at different strain levels at room temperature condition. Then, the samples were stretched under room condition at a strain level of 0%, 20%, 40%, 60% and 80%. The initial length of the sample is 20 mm and the samples were stretched until a maximum of 36 mm. For each strain level, the samples were set to stabilise for 30 seconds before the resistance was measured. For thermo-strain test (Figure 1(c)), the samples were stretched at different strain levels which are 0%, 20%, 40%, 60% and 80% followed by heating at room temperature (RT), 40°C, 60°C and 100°C for 30 seconds concurrently before deploying the Four-Point Probe for sheet resistance measurement.

In this study, the experiments were repeated three times. For each test, the samples were divided into five points to obtain accurate data collection as shown in Figure 2. Three readings were taken at each point. A Four-Point Probe technique was performed to determine the sheet resistance of the SFCP. Surface morphology of the samples was qualitatively observed using SEM.

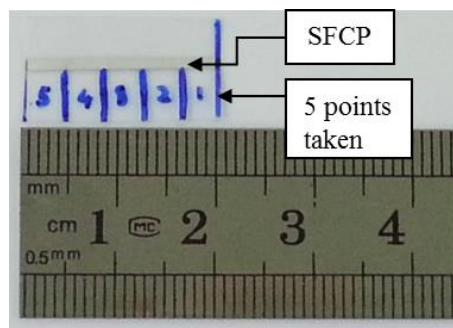


Figure 2. Sample of thermo-mechanical tests.

2.3.2 Wettability Test

In this experiment, the TPU substrate was cut into small pieces with a dimension of 20 mm in length and a nominal thickness of 0.15 mm. The samples were then washed with a detergent solution before ultra-sonicated with distilled water. Then, the samples were dried at room temperature for 15 minutes. Wettability test was conducted on two sample states. In the first state, the samples were measured at room temperature (RT- 40°C). Then, in the second state, the samples were heated at different temperatures (40°C, 60°C and 80°C) before measuring the contact angle of samples. Uniform amount of droplets (5 µL) were dropped on the sample before measuring the contact angle. For every temperature, five samples were used and each sample was divided into 5 different points. Three replicates of contact angle were taken at each point to assure its accuracy and precision. The surface roughness of samples was also measured to confirm the factor affecting the wettability of the TPU by using Profilometer Surfatest SJ-410. Three measurements of surface roughness were taken for each sample with a sampling length of 4.8 mm.

3. RESULTS AND DISCUSSION

3.1 Thermal Properties of TPU

To study the effect of temperature and strain on the SFCP sample, it is essential to learn the thermal properties of the substrate first. Hence, the DSC analysis was conducted to classify the temperature of glass transition (T_g), melting point (T_m) and recrystallization (T_r) of TPU. This information is the key to determine the operating temperature of the oven. The operating temperature must be set lower than T_g of TPU to ensure that the heating will not modify molecules movement that greatly restricted by intermolecular interaction.

Figure 3 illustrated the result of DSC analysis on TPU. The DSC analyses showed that the thermal properties of TPU inhibit the glass transition (T_g) at 105.1°C. The results obtained is greater than RT and showed that the TPU possesses thermoplastic properties. A small melting peak (T_m) was observed at 156.6°C representing a temporary arrangement which associated with crystallites which demonstrate TPU is operating as an amorphous thermoplastic. Thus, the TPU has possesses low crystallization degree and relatively soft from a soft segment that formed either from polyesters or poly (ether glycols) which contribute to the flexibility and elastomeric properties of TPU [8,9]. In summary, TPU exhibits both thermoplastic and elastomer behaviour which prove that TPU belongs to the thermoplastic elastomer. Based on these thermal properties analysis results, the heating temperature of TPU is set at 40°C, 60°C and 80°C.

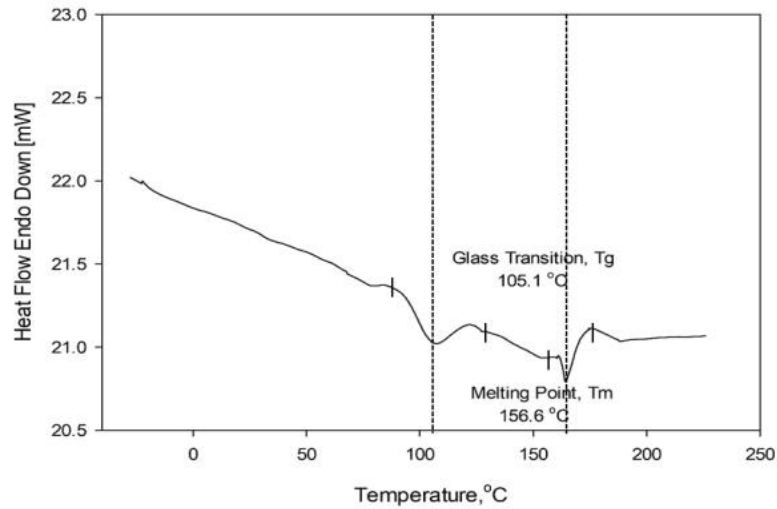


Figure 3. Thermal analysis of TPU by using DSC.

3.2 Effect of sheet resistance at various temperature

Effect of sheet resistance at various temperature of SFCP ink deposited onto the TPU substrate is depicted in Figure 4. The average sheet resistances for the samples were 0.09 $\Omega/\text{sq.}$, 0.12 $\Omega/\text{sq.}$, 0.11 $\Omega/\text{sq.}$, and 0.05 $\Omega/\text{sq.}$, for sample subjected to RT, 40°C, 60°C and 80°C, respectively. It should be noted that the decrease in resistivity indicates an increase in conductivity of SFCP. The result shows the initial resistance increases from RT to 40°C and starts to decrease after the temperature reach 40°C. This observation is due to the thermal expansion of Ag conductive particles in the SFCP resulting in higher percolation threshold that leads to expansion of Ag particles due to the formation of the conductive network in metal-filled polymer composite [10].

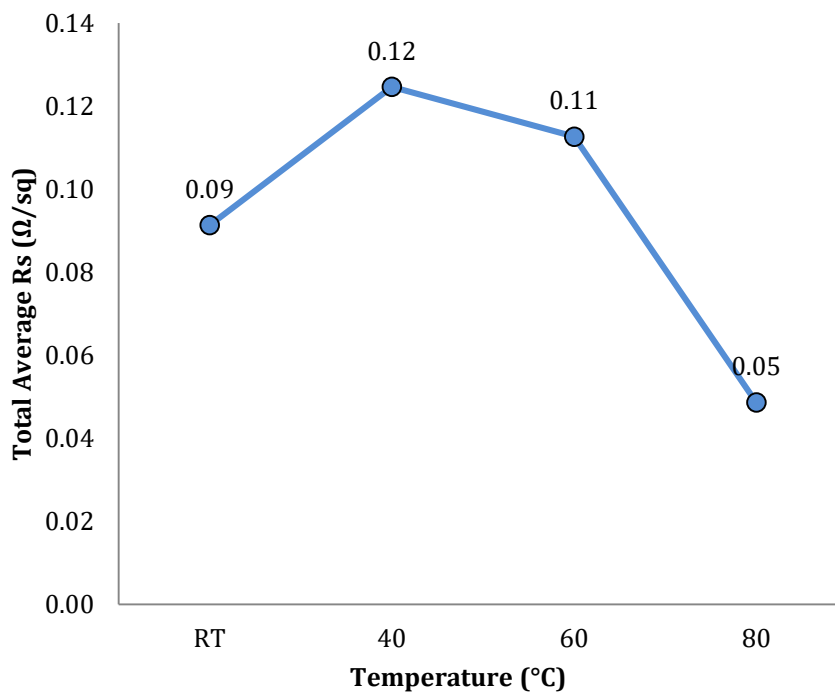


Figure 4. Average sheet resistances at various temperatures.

The surface morphology of SFCP was further analysed qualitatively using SEM and shown in Figure 5(a) to 5(d). The results reveal that the surface morphology structure of the SFCP is different for every set of temperature ranging from (a) RT to (d) 80°C. Visual observations on the SEM images clearly show that as the temperature increase, Ag particles was becoming expanded as the average size of particles increases from 2.74 μm to 3.98 μm which lead to the gap between particles to decrease. Small gaps in between particles create conductive paths which allow the ease of electron movements as explained by Merilampi *et.al* [11]. This occurrence shows that the morphological changes of the Ag particles associated with an increase in heating temperature can be directly correlated to the change in resistivity of the SFCP as a function of temperature. The enlarged of Ag particles increase the surface contact between particle to form an interconnected network of particle which reduces the resistivity effectively increase the conductivity.

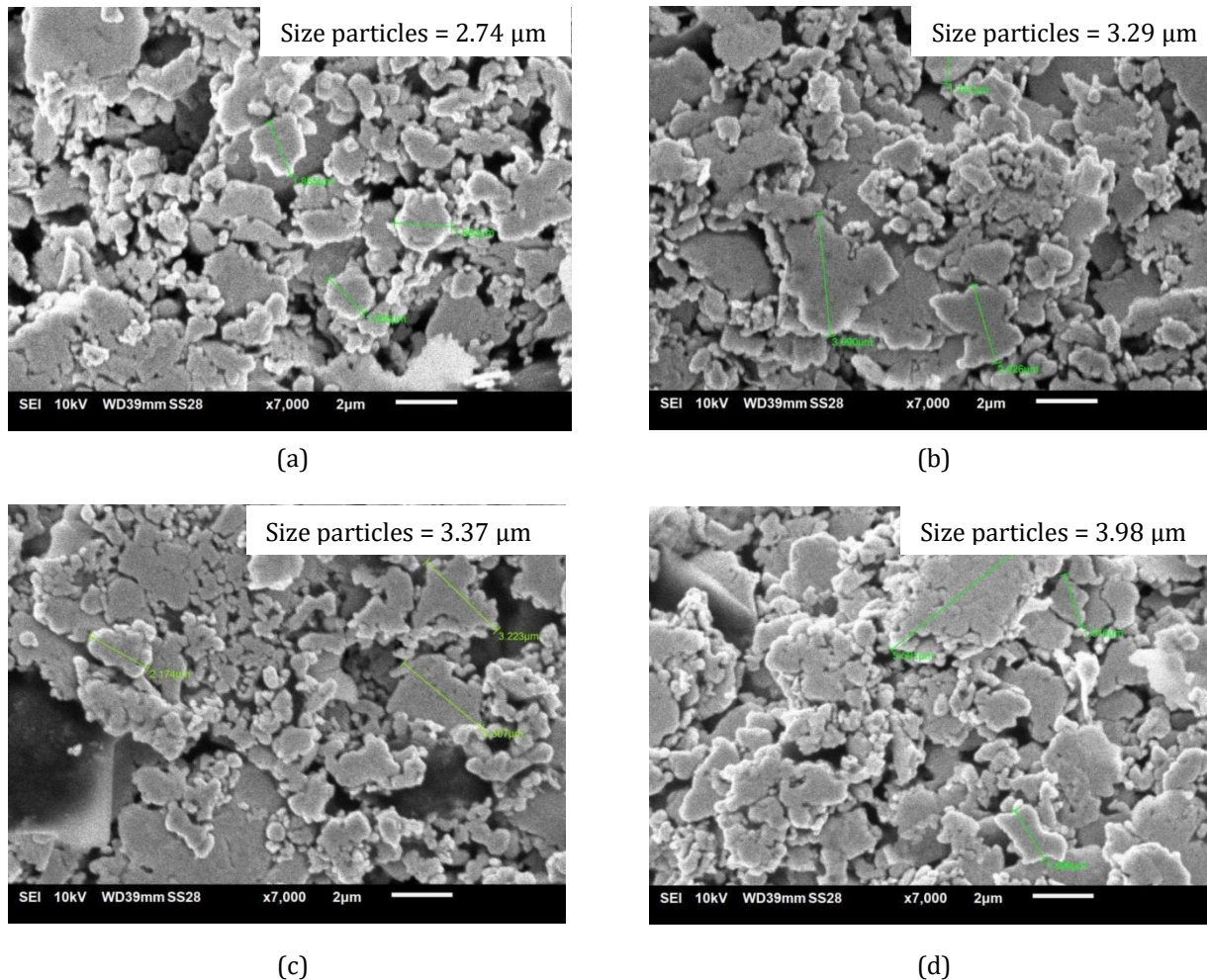


Figure 5. SEM micrograph of SFCP for (a) RT-25°C, (b) 40°C, (c) 60°C, and (d) 80°C at x7000 magnification.

3.3 Effect of sheet resistance on different strain level

The effect of sheet resistance on strain level (0%, 20%, 40%, 60%, and 80%) were depicted in Figure 6(a) - 6(e). In Figure 6(a), the image of the surface morphology sample from Axioscope 2MAT Optical Microscope before applying strain shows that the SFCP ink has a smooth and even surface without any crack. However, when the strain was applied at 20% without temperature, the formation of cracks is visible as shown in Figure 6(b). The crack formation continues 40% of strain (Figure 6(c)) and increases rapidly at 60% of strain (Figure 6(d)). The larger crack area is shown in Figure 6(e) with the largest formation of a gap between the Ag particles, resulting in

less contact surface between the particles as well as less conductive paths created on the TPU substrate. The initial crack occurs at the lower strain and increases rapidly at the highest strain.

Table 1 shows the results of the average value of sheet resistance (Ω/sq) at five different percentages of strains. The finding shows that the average sheet resistance of SFCP is directly proportional to the percentage of the applied strain which increases the percentage of strain, hence increases the average of sheet resistance. According to the Christopoulos and Tsamasphyros, the change of electrical conductivity subjected to mechanical strain is due to the change in the morphology structure of materials [12]. The electrical conductivity of the SFCP is achieved by a conductive network created by the contacts of the Ag particles in the polymer matrix. Thus, by applying strain to the samples will change the original length of the material while changing the gap between Ag particles. Thereby, changing the overall electrical resistance. The deformation caused an alteration in the gap of the inclusions which affects the contact between the conductive particles. A study by Cairns and Crawford shows that the increase in sheet resistance of the samples is due to the cracking that occurs during stretching of the samples [13]. Based on Table 1, the lowest value of sheet resistance is $0.59 \Omega/\text{sq}$. and was found at 20% level of strain due to a smaller number of cracks appeared on the surface of SFCP. The highest value of sheet resistance is $10.13 \Omega/\text{sq}$. when the sample was stretched at the 80% of strain-level due to the larger and higher number of cracks which appeared on the SFCP.

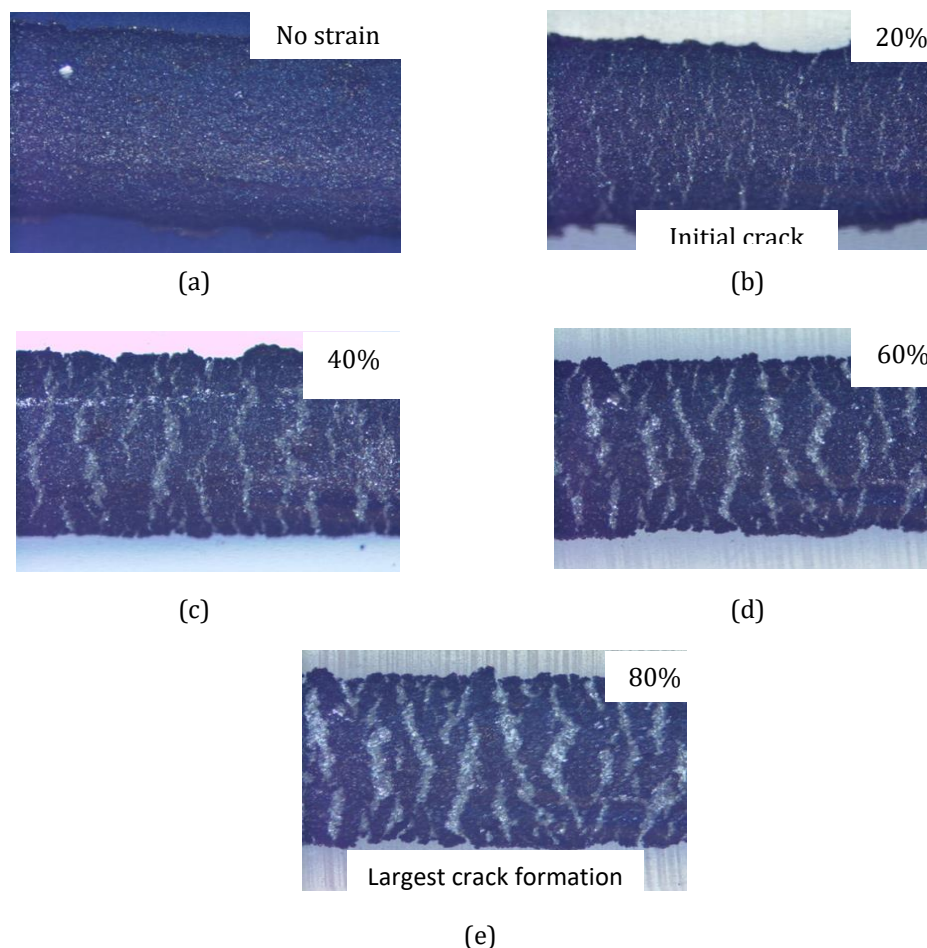
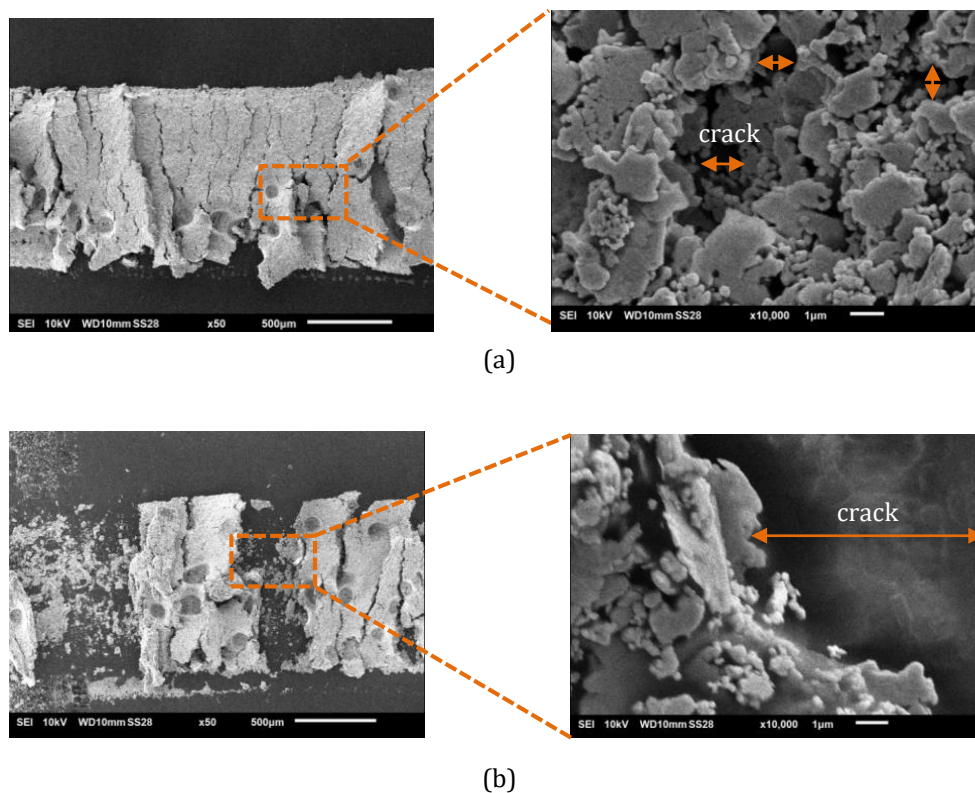


Figure 6. Surface Morphology from Axioscope 2MAT Optical Microscope of different strain level (a) before strain test, (b) 20%, (c) 40%, (d) 60%, and (e) 80%.

Table 1 Average sheet resistances values at different percentages of strain

Percentage of strain (%)	Average sheet resistance (Ω/sq)
0	0.10
20	0.59
40	2.62
60	4.65
80	10.13

The SEM analysis shown in Figure 7 further reveals the gap formation at the higher and lower strain. Therefore, the formation of crack on the SFCP surface was found as a factor that causes the difference in resistance as a function of strain which affects the rate of electron flow between the Ag particles resulting in less amount of electrical chargeable to move past the SFCP surface.

**Figure 7.** SEM analysis of (a) initial crack (b) largest crack formation.

3.4 Effect of Sheet Resistance on Various of Thermo-Strain

The correlation between thermo-strain effects with the conductivity of SFCP has been investigated and presented in Figure 8. Exposing SFCP to the highest temperature of 80°C and maximum strain level (80%) exhibited the lowest resistance compared to the samples subjected to other temperatures. At the higher temperature of 80°C, the Ag particles were expanded and resulted in increasing of the size of its molecules. This occurred due to an increase in its kinetic energy [14].

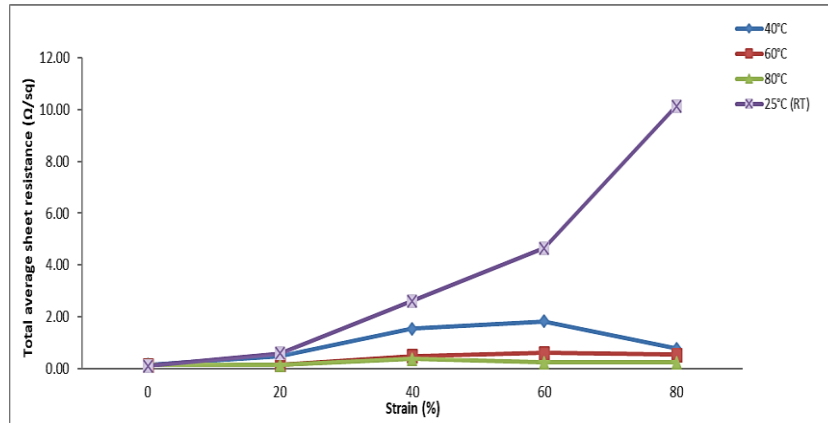


Figure 8. Average sheet resistances at various thermo-strain.

A study by Bridge *et al.* [15] stated that physical contact among particles is not necessary, as long as the gap between particles is close enough (~ 10 nm) to allow electron hopping across the gap, it will form network path of electrical conduction. Therefore, the increase of the size of the Ag particle will reduce the gap that forms when stretching the samples which resulting in the decrease of sheet resistance even after stretching the samples at a high strain level. In some occurrence, when the polymer matrix composite is strained, it also can cause the modification of the 3D network produced by the conductive particles, the decrease of the connection between particles, the addition in the inter filler gap, the delamination, and reorientation of particles and the reduction in the volume fraction of the filler material as the material is extended breaking [16-19].

3.5 Wettability and Adhesion Properties of TPU Substrate

Adhesion properties of TPU substrate can be affected by the crack formation on the SFCP surface. Poor adhesion between SFCP surface and TPU was believed to lead to the crack formation during stretching of the sample [11]. Wettability was carried out and the result was tabulated in Table 2. The value of the contact angle of TPU at room temperature was observed at the value of $95.5 \pm 1.6^\circ$. This value indicates that TPU exhibits hydrophobic behaviour with contact angle higher than 90° at room temperature. This occurrence could be explained with the correlation between contact angle and surface energy. For a solid surface that has weaker surface energy than the surface tension of the liquid, the liquid droplet tends to keep its shape better due to low interfacial tension between the solid surface and liquid [20]. Surface energy for TPU does not surpass more than 40 mJ/m^2 [21,22] and was considered as low surface energy which indicates that TPU has higher surface tension and low wettability [23]. It also indicates that the TPU surface at room temperature has low adhesion due to the low contact area between the adhesive like SFCP and the substrate resulting in low interacting force between them [4]. Exposed the TPU to the temperature of 40°C , 60°C and 80°C generally shows that the contact angle of TPU is directly proportional to the temperature as shown in Figure 9. After heating at 40°C , 60°C and 80°C , the contact angle of TPU increases from 65.5° to the 99° , 101° , and 103° , respectively.

Table 2 Contact angle results for TPU at room temperature

Point	Contact angle, $^\circ$
1	96.5
2	97.1
3	96.5
4	94.3
5	93.3
Mean \pm std. deviation	95.5 ± 1.6

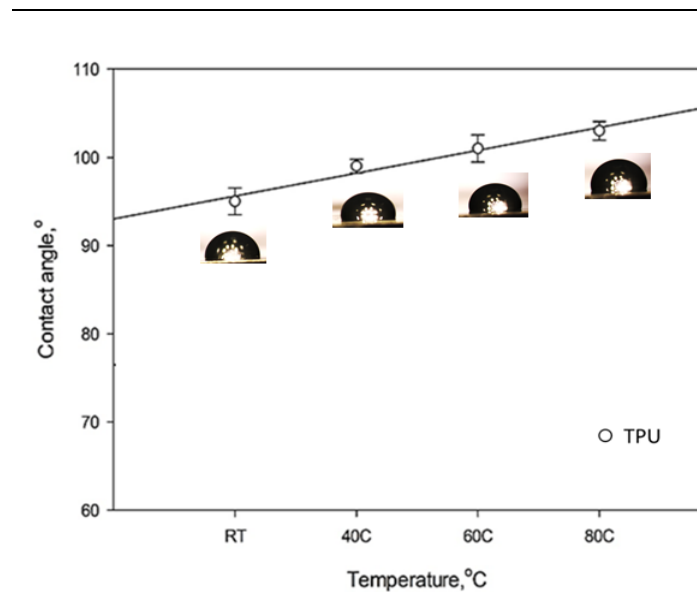


Figure 9. Contact angles of TPU at room temperature (RT), 40°C, 60°C, and 80°C.

Several studies revealed that surface roughness also highly influenced the value of contact angle and surface energy [24,25]. The connection between surface roughness and contact angle is best described by Wenzel model and Cassie-Baxter model. Wenzel Model can be conveyed as;

$$\cos \theta_w = R_f \cos \theta_o \quad (1)$$

Where θ_w is the contact angle on the rough surface, θ_o is the contact angle on the flat surface and R_f is a roughness factor.

From the Eq. (1), the roughness factor R_f will influence the θ_w based on the chemistry of the surface. This means if the surface exhibits hydrophilic properties, the increase of R_f will cause the surface to become more hydrophilic. While, for the hydrophobic surface, the increase of R_f will cause the surface to become more hydrophobic [24-26]. Meanwhile, the Cassie-Baxter model states that the increase of air traps between the water droplet and material surface will enhance the wettability. The model can be expressed as;

$$\cos \theta_w = R_f \cos \theta_o - f_{LA}(R_f \cos \theta_o + 1) \quad (2)$$

Where f_{LA} is known as the fractional of a flat area between the liquid-air interfaces under the droplet.

The model indicates that the increase in f_{LA} will decrease the contact area between solid-liquid therefore increase the θ_w . To examine the effect of this factor on the sample, the analysis of roughness was performed. The increase of surface roughness indicates that the surface of TPU becomes rougher after heated. This phenomenon will cause the air trap between the rough surfaces to increase as explained in details in a previous study [27]. Thus, it can be summarized that the contact area between a liquid droplet and TPU surface decreases when increasing the temperature up to 80°C which causes the adhesion on TPU substrate become more worst at higher temperature especially when applied strain. In other words, the wettability of the surface is affected by the difference in the surface roughness that may influence the adhesion between adhesive and substrate.

4. CONCLUSION

SFCP ink was applied on TPU substrate and from the experimental data, the thermo-mechanical and adhesion performance of SFCP were characterized. The results of this investigation show that sheet resistance of SFCP increased with an increasing strain and decrease with the increase of temperature due to the crack formation against strain. The initial crack occurs at the lower strain and increases rapidly at the highest strain. However, the sheet resistance decreased at high temperature and strain (80°C at 80%). It happens because the presents of temperature allow the Ag particle to expand, filled the gap and formed a network path for electrical conduction. However, the TPU shows low wettability that exhibits poor adhesion between SFCP ink and TPU substrate due to decreasing contact area between adhesive and substrate that causes the surface has low surface energy when exposed to variation of temperature. Besides, the thermal and thermo-strain tests are known as sintering process that use to improve the conductivity and stretchability for SFCP ink. The SFCP ink was exposed to heat or pressure to the removal of organic materials from ink and it helps conductive particles to expend and attach together. However, the sintering process for the SFCP ink must be applied at low sintering temperature to maintain stretchability and adhesion of SFCP.

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