Nanoindentation of Graphene Reinforced Epoxy Resin as a Conductive Ink for Microelectronic Packaging Application

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ABSTRACT

Conductive ink is a special type of ink which allows current to flow through the ink. There are several varieties of conductive inks in the market and it is crucial to choose a suitable ink for the electronic applications. Graphene material is chosen to replace the current ink due to its promising properties that have been explored by many researchers. This paper aims to investigate the effect of temperature and percentage of graphene ink on hardness and Young's modulus of printed graphene ink samples. Samples were fabricated using a simple method involving formulating, mixing, printing and curing processes and the ink was printed on the glass slide substrate. The samples were cured at 160°C and 180°C for one hour. The mechanical properties of printed graphene ink sample were evaluated using Dynamic Ultra Micro Hardness (DUMH). All the measurements were done with the same force of indentation to avoid the possibility of perforation of printed graphene ink. The results show that higher curing temperature and percentage of filler loading give bigger Young's modulus and hardness of the printed graphene ink sample.

Keywords: Graphene Nanoplatelets, Nanoindentation, Hardness, Young's Modulus, Conductive Ink.

1. INTRODUCTION

Conductive ink can be printed directly on a substrate or any flexible surface through a regular printing process and allows an electric current to flow through it [1]. The ink is usually applied to the substrate and slightly heated up to evaporate the solvent and bind the conductive particles together. It is a significant component for many applications, with the widespread use in photovoltaic cells, medical devices, membrane switches, as well as Radio Frequency Identification (RFID) chips and can be regarded as the next generation of the electronic device [2].

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Figure 1. Stretchable Conductive Ink based on screen-printed silver paste [3].

Moreover, conductive ink can replace the printed wiring and beneficial for simple circuitry that needs low-cost method. The stretchable conductive ink is flexible and expandable while maintaining high conductivity level. Basically, in preparing the effective conductive ink, the crucial components that need to be considered are compatible polymer binder and filler. Atif *et al.* [4] stated that the integration of nanofiller is a very effective strategy to increase the performance of the material itself. In this study, epoxy resin was selected as a polymer binder because it offered superlative mechanical properties, thermal stability, solvent resistance as well as ease of processing [4].

In addition, it is required for material that can hold other materials together to form a cohesive whole mechanically, either by adhesion or cohesion. Furthermore, to enhance the mechanical properties, particularly hardness, it can be obtained by reinforcing the polymer binder with a relatively small amount of nanofiller. The nanofiller can be metallic nanoparticles and carbon nanoparticles [5]. Among these nanoparticles, graphene has become an attractive option in the past decades due to its unique properties with a two-dimensional structure. Atif *et al.* [4] also stated that it had a large surface area (2630 m2g-1) and possessed excellent mechanical properties such as Young's modulus at 1×106 MPa and tensile strength of 130 GPa. It makes graphene as one of the strongest material available today [4]. This factor has led to the exploration of graphene reinforce epoxy resin in various applications nowadays.

The effectiveness of graphene in enhancing mechanical properties has been investigated using the nanoindentation technique. In the last twenty years, nanoindentation was introduced as a method to determine Young's modulus and hardness of materials by studying nanomechanical response as a function of penetration depth [6]. Besides that, nanoindentation is also widely used to study the displacement of material under specific loads to produce load-displacement curves. This research attempts to evaluate whether the curing temperature and different weight percentage of filler loading influence the morphological and mechanical properties.
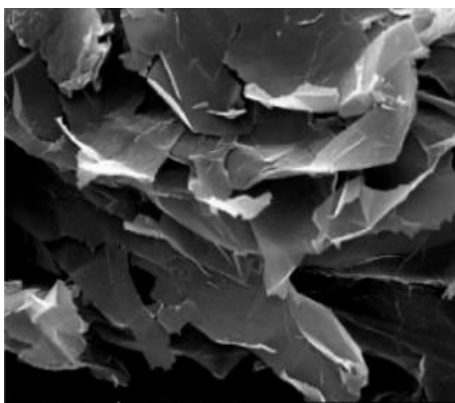

Figure 2. SEM image of Graphene nanoplatelets.

2. MATERIAL AND METHODS

Graphene nanoplatelets with the surface area of 500 m2/g were used as the main filler in this study. Epoxy resin and hardener were used as a binder to bind the particles and harden the mixture, respectively.

2.1 Sample Preparation

The fabrication of conductive ink involves formulating the ink composition, ink sample preparation, print the ink on the compatible substrate and curing the ink at the specific time and temperature. In this study, the sample was cured in one hour at two different temperatures; 160°C and 180°C. In the beginning, four samples of conductive ink were prepared; 5, 10, 15 and 20 wt% of graphene with the hardener in the ratio of 100:30. The ink was prepared by manual mixing, which involved stirring process that took about 10 minutes at room temperature by using a glass rod. Stirring plays an important role in ensuring the uniform distribution of epoxy in the mixture and it can break up the agglomerates of graphene and epoxy resin to produce high dispersed graphene/epoxy dispersion.

Table 1 The composition of the ink

Sample	Filler		Binder		Hardener	Total (g)
	(%)	(g)	(%)	(g)	(g)	
1	5	0.1	95	1.9	0.57	2
2	10	0.2	90	1.8	0.54	2
3	15	0.3	85	1.7	0.51	2
4	20	0.4	80	1.6	0.48	2

Once the dispersion process was completed, the ink was printed on a glass slide (25 mm × 75 mm) as shown in Figure 3 by using a screen printing method [7]. The glass slide was practically used as a based substrate to find the best formulation of ink in this experiment. During the curing process, it produces highly-cross linked microstructure that provides high modulus and strength, good resistance to creep and good performance at elevated temperature [8]. Then, the cured sample was cooled down slowly to room temperature inside the oven. The sample preparation for the printed ink is shown in Figure 4.
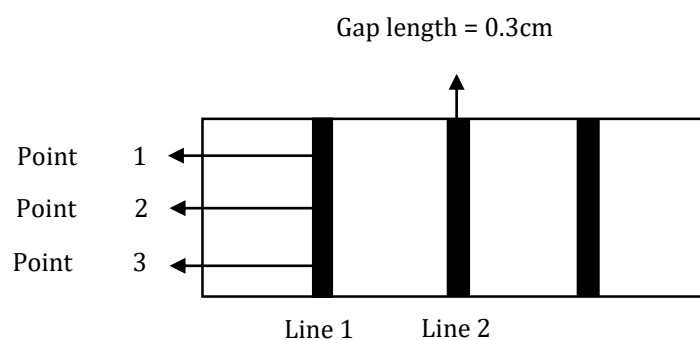

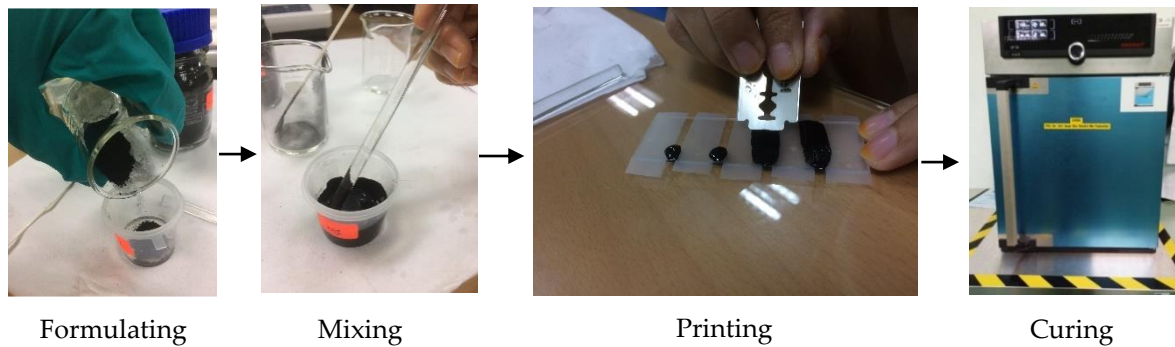**Figure 1**. The printed graphene ink on a glass slide as a substrate.

| Formulating | Mixing | Printing | Curing |

Figure 2 Sample preparation.

2.2   Characterization

The characterization of composite consists of the analysis of their basic morphological features and the determination of mechanical properties.

2.2.1   Mechanical Properties

Nanoindentation analysis was carried out by using Dynamic Ultra Micro Hardness (DUMH) testing. Evaluation of hardness and elastic modulus were in accordance with ISO Standard 14577-1 Annex A. In this study, the parameters were set for 5 kN load and 5 seconds holding time. During each test run, a personal computer collected and stored data for the load and displacement as the indenter was driven into the sample. Then, the raw data was used to construct the load-displacement graph. Twelve indentations were made for each sample with three indentations for each point and the mean values were calculated by averaging the hardness and recorded. Since the mechanical properties extracted from the nanoindentation were sensitive to the tip geometry, the tip area function had to be calibrated before determining the mechanical property accurately [10].

Figure 3. The sample was set on the stage.

2.2.2   Morphological Properties

The light microscope provides the measurement of particles shape and size, morphology and the disposition of nanoparticles. In this experiment, 2000x magnification lens was used to capture the microstructure image of the ink.

3. RESULTS AND DISCUSSION

3.1 Mechanical Characterization

Nanoindentation analysis was carried out using the method described by Dong [11]. Significantly, the two mechanical properties most frequently measured were Young's modulus and hardness [12]. As the indenter was driven into the material, both elastic and plastic deformations caused the formation of hardness. After the indenter was withdrawn, only the elastic portion of the displacement was recovered, thus this recovery enabled the determination of the elastic properties of a material. Therefore, the first step of the measurement was preparing the sample by mounting it on a sample disk [13]. The load-displacement graph in Figure 8 and 9 show the typical load-indentation depth curve obtained by nanoindentation for screen printed graphene ink cured at different temperatures – 160°C and 180°C for one hour. It can be seen that the curves are similar in shape but the indentation and elastic behaviour are different.

Table 2 The value of the maximum penetration depth for the sample.

Filler loading (wt%)	Force	h_{max} (um)			
		160°C	Error Bar	180°C	Error Bar
5	19.63	2.104	0.1052	1.997	0.09985
10	19.63	1.935	0.09675	1.795	0.08975
15	19.63	1.919	0.09595	1.725	0.08625
20	19.63	1.830	0.0915	1.610	0.0805

Figure 6 encapsulates the maximum penetration depth from all the printed graphene ink sample starting from 5 wt% to 20 wt% at two different curing temperatures. It is clearly shown that the higher the percentage of filler loading, the lower the penetration depth. Lower penetration depth indicates that the printed graphene ink is getting hardened.
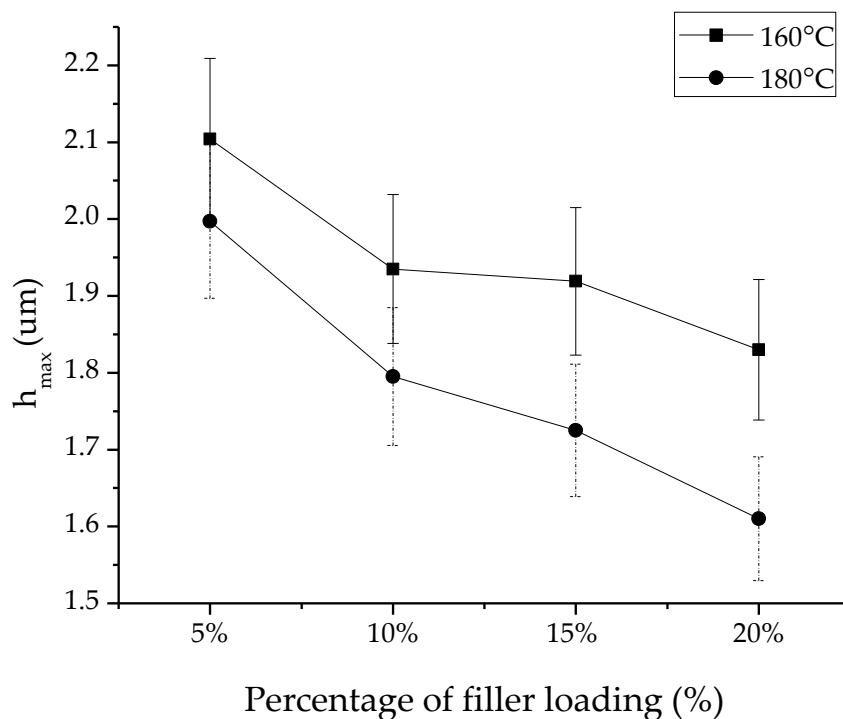

Figure 4. The graph of the maximum penetration depth for nanoindentation.

Figure 7 represents the load indentation depth curve at 160°C. As a result, when the ink was being indented, 5 wt% deformed much easier as compared to other three filler loadings. Hence, among all four different filler loadings, the indentation of 5 wt% yields the maximum penetration depth, h_{max}=2.104 um, at the peak load of 19.63 mN. In contrary, the minimum indentation is obtained from 20 wt% that yields h_{max}=1.832 μm at the similar peak load. Therefore, it is reasonable to infer that, the surface condition of the ink for 5 wt% filler loading is softer as compared to the other three samples. The analysis was supported by previous studies conducted by Gong [14].
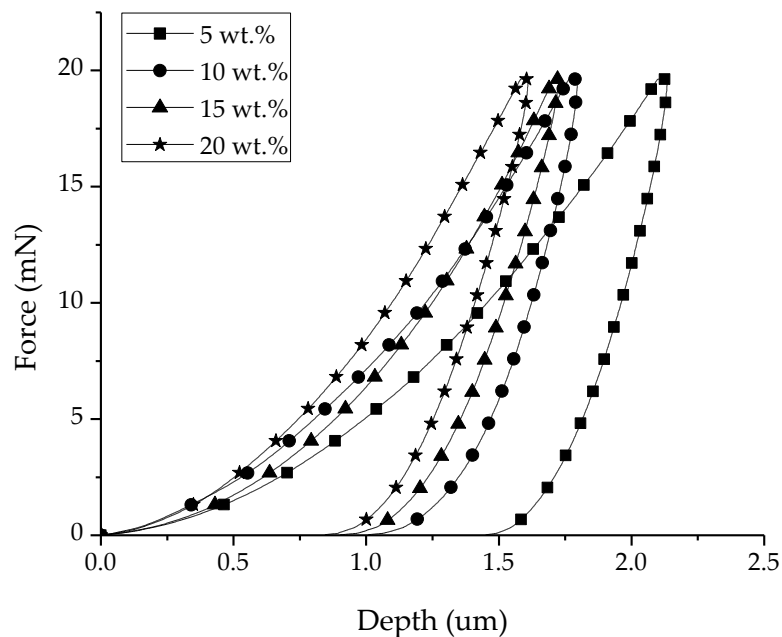

Figure 5. Typical load-indentation depth curve at 160°C.

On the other hand, Figure 8 shows the maximum and minimum penetration depth of the samples with different filler loadings. The maximum penetration depth occurs at 5 wt% with h_{max}=1.997 μm. Meanwhile, 20 wt% acquires minimum penetration depth with h_{max}=1.610 μm at the peak load of 19.63 mN. As a result, the surface of the ink for a lower percentage of filler loading yields a softer surface while for higher percentage filler loading yields a hardened surface. Figure 7 and 8 also clearly show that as the percentage of filler loading increases, the penetration of the indenter steadily decreases.
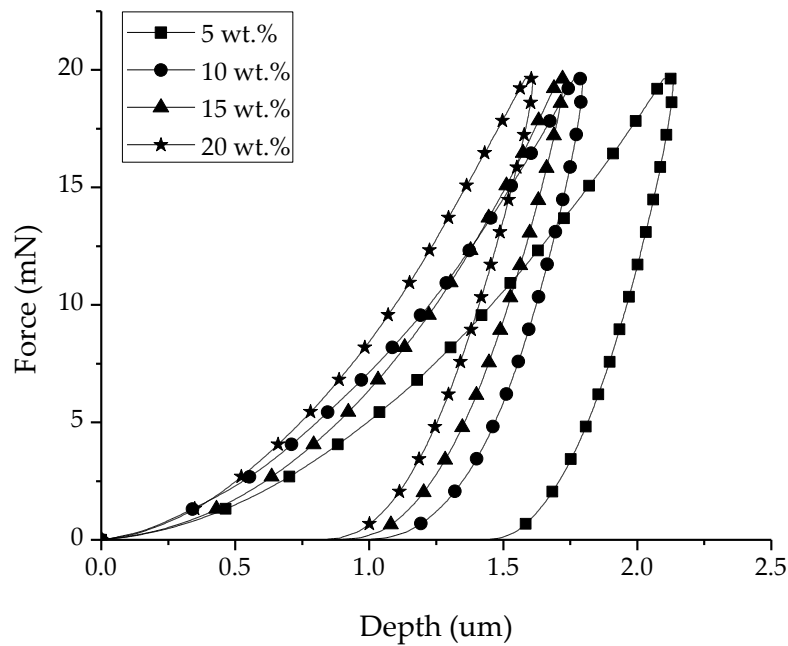
Figure 6. Typical load-indentation depth curve at 180°C.

Table 3 The results of Hardness and Young Modulus

Filler loading (wt%)	Hardness (GPa)		Young Modulus (GPa)	
	160°C	**180°C**	**160°C**	**180°C**
5	0.259	0.264	5.42	5.82
10	0.276	0.278	5.50	6.05
15	0.287	0.336	5.63	7.34
20	0.305	0.391	7.43	8.91

Based on Figure 9, when the curing temperature increases, the hardness level of the printed graphene ink sample also increases accordingly. For 160°C, the value increases in parallel with the increase of filler loading with 0.259 GPa to 0.305 GPa. While for 180°C, the value of hardness also increases from 0.264 GPa to 0.391 GPa. Similarly, this study is also consistent with the results of Chatterjee *et al.* [15] who reported an increase of approximately 0.266 GPa for the neat epoxy to 0.290 GPa for 20 wt% of GNP loadings [15]. In short, the nanoindentation results show an improvement in hardness for the sample at a temperature of 180°C. Therefore, hardness value has a similar tendency with sintering temperature. These increases are closely associated with grain growth at a higher temperature. More grain growth at higher temperature improves the mechanical properties. Moreover, the nanoindentation results confirm that the toughness of the ink increases when the curing temperature increases. Besides that, by considering the error bar, the addition of graphene contents does not seem to affect the hardness of the ink.
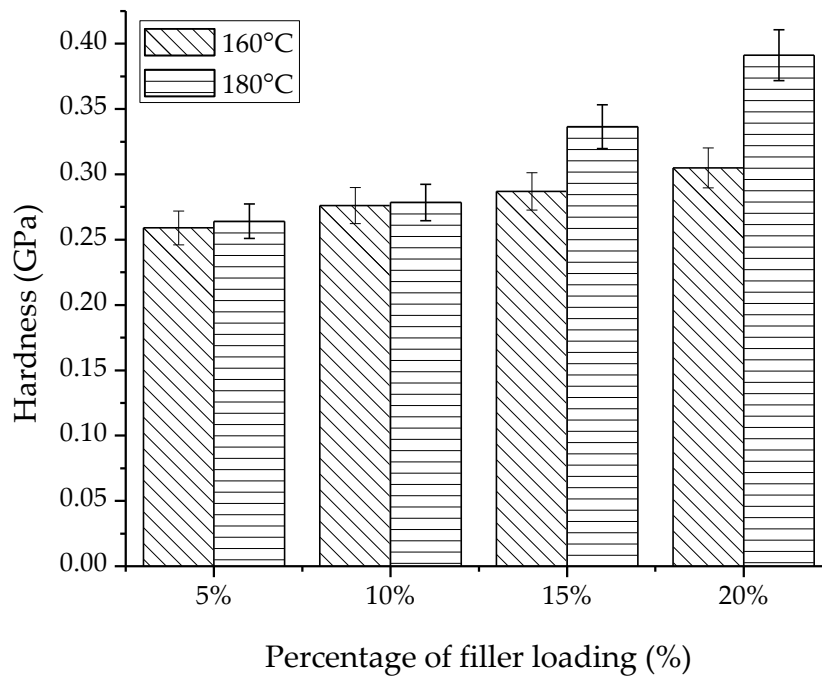
Figure 7. Hardness against a percentage of filler loading at two different temperatures.

Moreover, Figure 10 indicates the result of Young's modulus of the samples at two temperatures. As can be seen from Figure 9 and 10, as expected higher curing temperature leads to higher hardness and Young's modulus of the printed graphene ink samples. It has been observed that Young's modulus for 180°C is higher with 8.91 GPa at 20 wt% filler loading as compared to 160°C with 7.43 GPa at similar filler loading. The elasticity begins to degrade when the curing temperature increases. This study assumes that, by adding the temperature, the properties of graphene ink will change from brittle to ductile. Therefore, graphene ink that cures at a higher temperature is likely to become more solid. The result of this study is compared to the findings of previous work. Chatterjee *et al.* [15] also reported that the values of Young's modulus obtained were approximately 3.9 GPa to 4.2 GPa, which were lower as compared to this study.
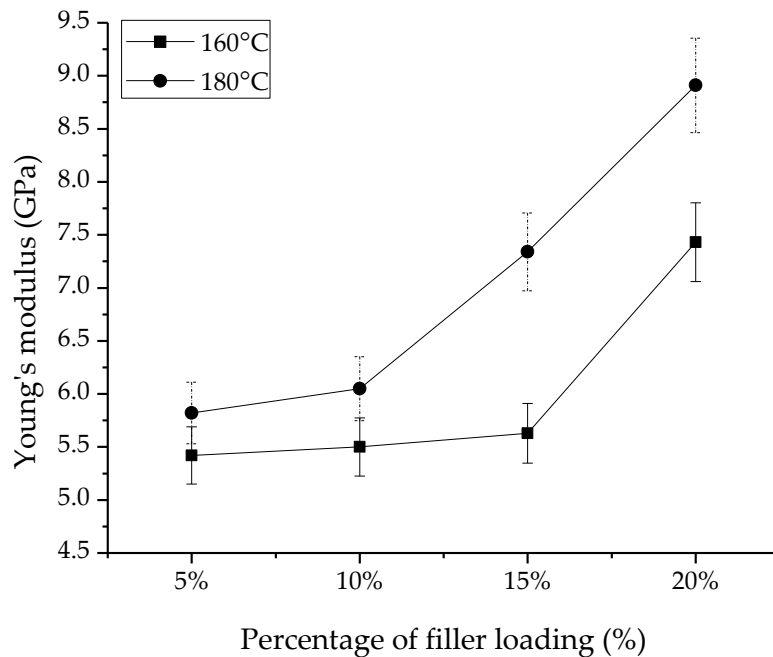
Figure 8. Young's Modulus against the percentage of filler loading at a different temperature.

3.2   Morphological Characterization

The basic morphological analysis was done using a light microscope to study the microstructure condition as well as the dispersion of the ink. Nanofiller dispersion is an important issue since graphene inherits the tendency to form agglomerates. It is due to strong Van der Walls attraction, large surface area and filler-filler interaction with the increase of weight percentage of graphene makes dispersion becomes even more challenging [16]. This also explains the limitation in improving the mechanical properties with the increase of nanofiller content. For this study, four different weight percentages of graphene were fabricated and there was no existence of resistivity for all the samples. Nevertheless, this study assumes that it happens due to the agglomeration effect. Agglomeration happens due to improper technique for stirring process during the sample preparation that can cause an ununiformed distribution of the mixture. It seems that all the sample are not well dispersed with the existence of the gap between the nanofiller as shown by the microstructure images in Figure 11 and 12. No electrical conductivity was produced due to the agglomeration effect. The agglomerates in the epoxy can lead to cracks initiation and it can propagate easily. Consequently, it reduces the strength of the composite. Therefore, this experiment was conducted to study this behaviour.

Additionally, microstructure images in Figure 11 and 12 show that the brighter image contains a low percentage of filler loading while the darker image contains a high percentage of filler loading. On top of that, low filler loading shows a smooth surface compared to high filler loading that shows a rough surface. After all, this research assumes that the black dot on the microstructure image indicates graphene while the rest is the binder and hardener. The gap between the graphene clarifies that there is no filler-filler interaction between the filler loading that leads to the existence of resistivity.
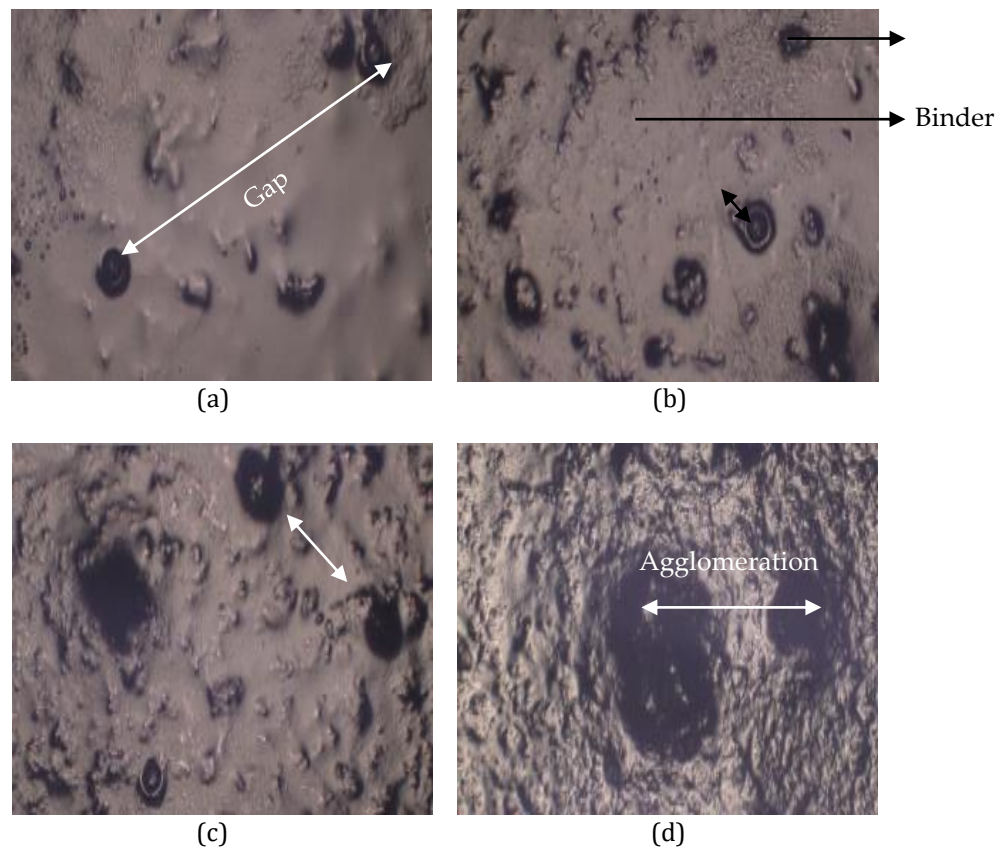
Filler

Figure 9. The sample that cure at 160°C (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, (d) 20 wt%.
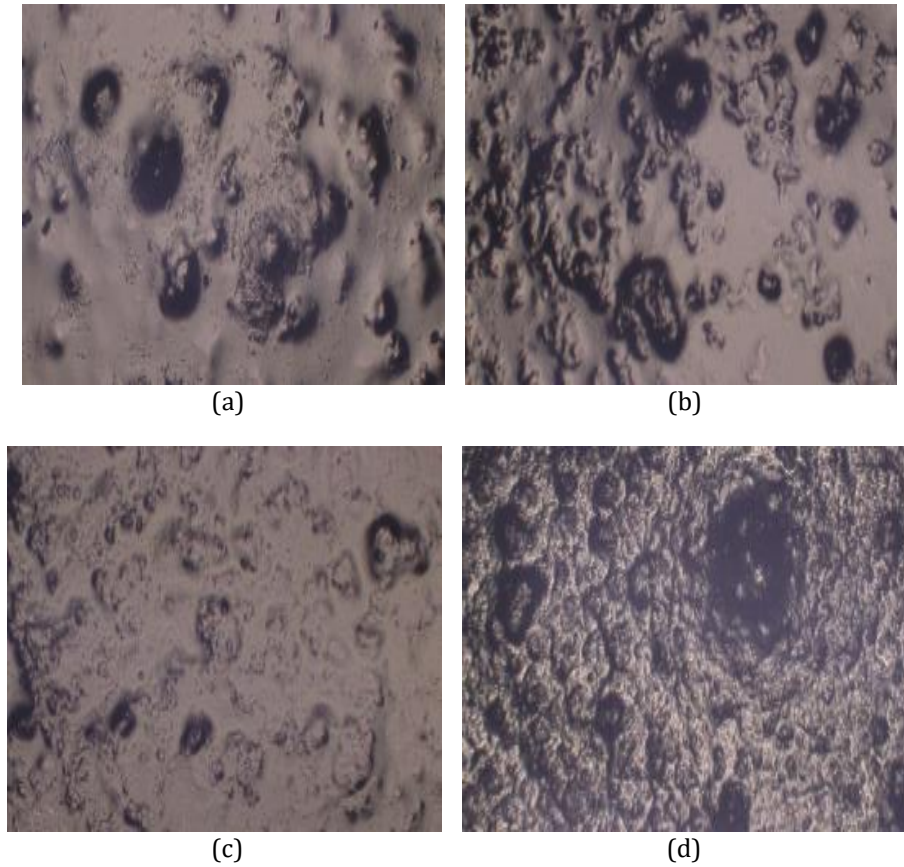

Figure 10. The sample that cures at 180°C (a) 5 wt% (b) 10 wt%, (c) 15 wt%, (d) 20 wt%.

4. CONCLUSION

In summary, a simple fabrication process had been used to disperse graphene through the epoxy resin to produce conductive ink. This study consists of the characterization of graphene/epoxy resin composite. The main objective is to investigate the mechanical properties when a low volume of graphene filler loading was added into thermosetting resin. The result showed that the mixture of the ink did not well dispersed during mixing method, therefore dispersion strongly influences the resistivity and microstructure of the graphene. Despite no resistivity, nanoindentation studies were conducted to identify the hardness and Young's modulus. Mechanical properties increased steadily with the incorporation of 20 wt% of filler loading. To sum up, this study indicates that, at higher filler loading, it offers a significant improvement in mechanical properties. However, the hypothesis is that further improvements are needed with an increase of graphene filler loading content to obtain homogeneous conductive ink. A network of well-dispersed graphene can provide a conductive path to produce resistivity and leads to high conductive ink.

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