

PREPARATION AND CHARACTERIZATION OF NANOSIZED GRAPHITE BASED THICK FILM FOR FLEXIBLE ELECTRONICS

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ABSTRACT

This paper presents results of study on graphite thick film paste using linseed oil as organic binder and nanosized graphite powder. First, graphite powder is milled for 1 hour to obtain nanosized powder. Next, graphite nanopowder is mixed with organic vehicle which consists of linseed oil, m-xylene and α -terpineol. Samples are prepared to study the morphology and electrical properties of the paste when subjected to different firing temperature, and also adhesion to flexible kapton film. Paste samples were screen printed onto kapton film as substrate, dried and fired at different temperatures of 300°C and 400°C respectively. Microscopic images of the samples were observed to determine good dispersion of the active powder with the organic vehicle. Based on the results, the paste with linseed oil as organic vehicle showed good adhesion to the substrate with low firing temperature at 300°C, but has high resistivity thus not having a good conductivity. Thick film with firing temperature 400°C has good morphology and conductivity, therefore higher temperature gives good result in terms of electrical properties. Longer firing holding time also helped to improve the conductivity of the graphite thick film.

Keywords: thick film; organic vehicle; screen printing; graphite; linseed oil; flexible

INTRODUCTION

Flexible circuits are popular due to its diversity in application as well as the design. Flexible circuits have served in a wide variety of demanding applications for a long period of time. Their versatility as an interconnection method is still deemed unmatched by other techniques. The trend is expected to continue as more and more engineers become familiar with flexible circuit technology's many benefits. The benefits of using flexible circuit technology includes reduction in package size and weight, dynamic flexure of the circuitry, compliant substrate for surface mounting and many others [1].

Sensors, particularly pressure sensors' manufacturing can benefit from this technology as they are currently serve as important element in robotics and medical devices.

Graphite is an allotrope of carbon, and can be produced as natural graphite or synthetic graphite. Graphite is widely used as pencil leads, as well as the anode of batteries. Graphite has a layered, planar structure. In each layer, the carbon atoms are arranged in a honeycomb lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm [2]. Graphite can conduct electricity due to the vast electron delocalization within the carbon layers, or which the phenomenon is called aromaticity. These valence electrons are free to move, therefore are able to conduct electricity. However, the electricity is primarily conducted within the plane of the layers. The conductive properties of powdered graphite [3] allows its use as pressure sensor in carbon microphones. Meanwhile, graphite thick films has been studied and used extensively as working electrodes for electrochemical analysis [4, 5], and also as printed resistor [6]. PVC-graphite composites have been reported to have good electrical properties with longer curing time and thermal cycling [7]. Another research group also reported on the preparation of lead-free graphite paste, which uses lead-free low-melting glass binder to address the restriction on using lead contained materials [8].

This project studies on the preparation of graphite thick film using nanosized graphite powder and without the use of glass binder, instead using linseed stand oil as organic vehicle to enable rapid drying and adhesion to substrate at low firing temperature. Linseed oil is also known as drying oil, which is widely used as painting medium. Its characteristics made the oil suitable for thick film since the boiling point is 343°C. This work also aims to achieve good electrical properties of the thick film with low firing temperature.

EXPERIMENTAL

The starting graphite powder used is graphitized carbon powder from Sigma-Aldrich USA. To obtain nanosized powder, the graphite powder was milled using high energy ball milling (HEBM) method for 1 hour. The microstructure of unmilled and milled graphite powder was observed using FESEM to confirm particle size reduction after milling was done. Next, the milled graphite powder is mixed with prepared organic vehicle, which consists of linseed stand oil, m-xylene and α -terpineol. The weight ratio of graphite powder and organic vehicle is set to 30:70. The mixture is then stirred using magnetic stirrer with speed of 250 rpm at 40°C for 3 hours to obtain a homogeneous paste. The paste viscosity is measured using rheometer to observe viscosity change over time and at different shear rate, while thermal analysis was done using TGA. The paste is then screen printed onto a 5-mil Kapton film as a flexible substrate, dried and then fired at different temperatures of 300°C and 400°C respectively, and different firing holding time to study the effect of firing temperatures to the properties of the thick film. Morphology of all samples was observed using FESEM, while EDX was done to confirm the elements found in the thick film. Finally, the sheet resistance of the sample is measured to observe the change in resistivity related to the various firing time and

temperatures.

RESULTS AND DISCUSSION

The FESEM images of the unmilled graphite powder are shown in Figure 1, while Figure 2 shows the images of graphite powder after being milled for 1 hour. As can be observed from the images, the 1-hour milling of the powder has decreased the particle size to few hundreds of nanometer scale. There are still, however, large grains which are visible in the images, showing that the milling did not entirely crushed the graphite powder in uniform. In order to completely mill the graphite to nanometer scale, more time is needed for the milling to completely grind the powders to nanoparticle sizes.

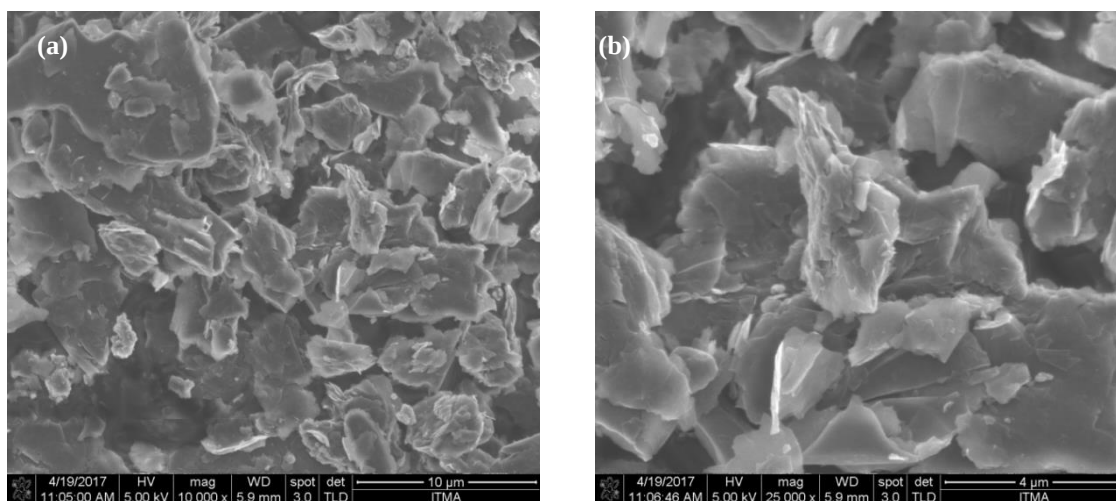


Figure 1: FESEM images of unmilled graphite powder: (a) at 10,000 magnification, and (b) at 25,000 magnification

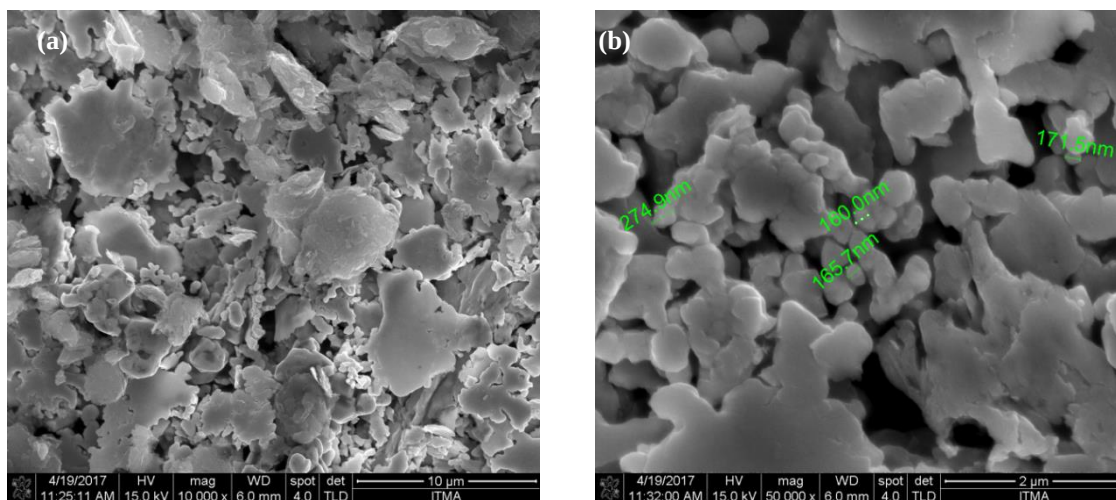


Figure 2: FESEM images of milled graphite powder: (a) at 10,000 magnification, and (b) at 50,000 magnification.

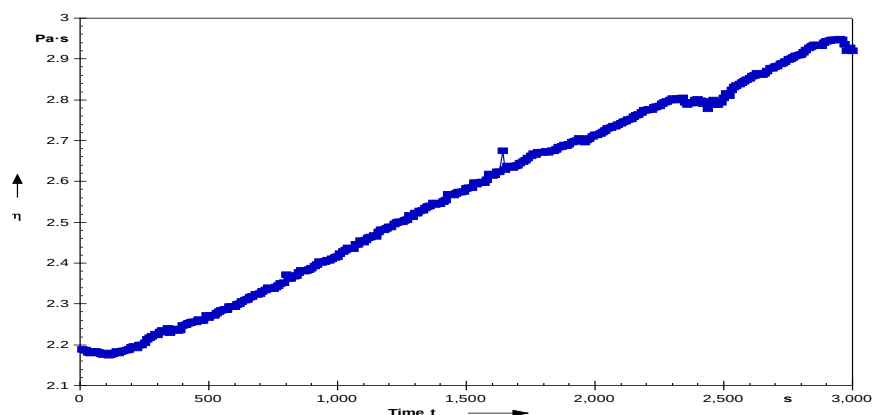


Figure 3: Viscosity versus time of milled graphite thick film paste for 3000 sec

Figure 3 exhibits the viscosity of graphite thick film paste using milled graphite powder over time span of 3000 seconds with fixed shear rate at 100 s^{-1} . As can be observed from the graph, the viscosity of the paste increased steadily over the time. This phenomenon can be related to the nature of linseed oil which is also known as drying oil, of which the oil is able to dry off or polymerizes at room temperature. The increase of viscosity, however, is not significant, of which the percentage is 4.56% after 600 seconds, 21.9% after 1800 seconds, and finally total increase percentage at 33.3% at 3000 seconds.

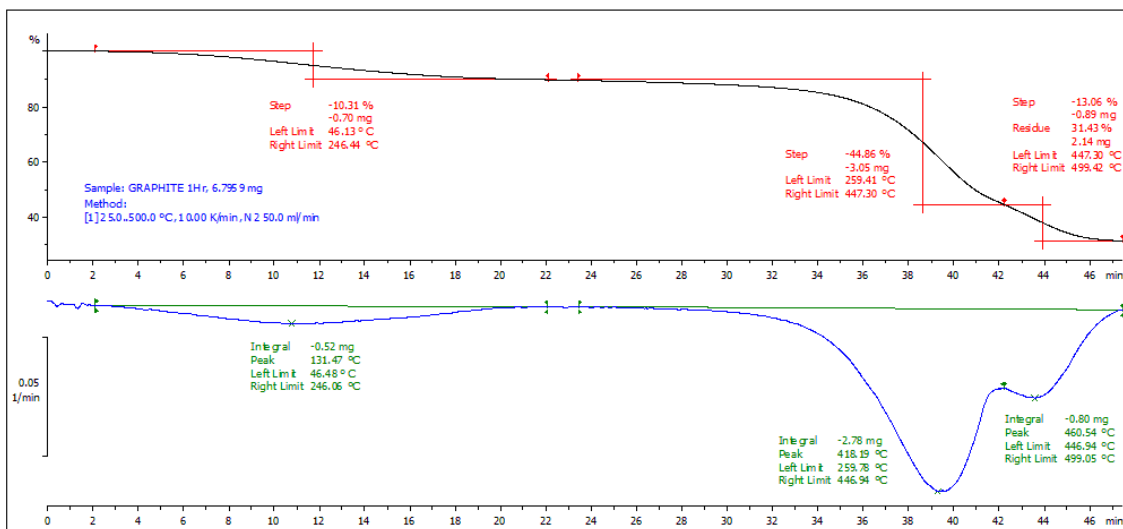


Figure 4: TGA result of milled graphite thick film paste (30 - 500°C)

Figure 4 shows the thermal properties of graphite thick film paste from 30°C until 500°C. The first phase of decomposition, which peaked at 131°C, resulted from the removal of non-volatile phase of the paste, which consists of m-xylene and α -terpineol. At 250°C, the volatile phase which is linseed oil started to evaporate, and continued to decompose until reached 500°C, when all organic vehicle has totally decomposed and

the powder is left as residue. The thermal analysis can help in determining the optimized firing temperature, of which high temperature of 500°C may not be suitable as firing temperature due to all organic binder has evaporated therefore leaving no element to bind the powder to the substrate.

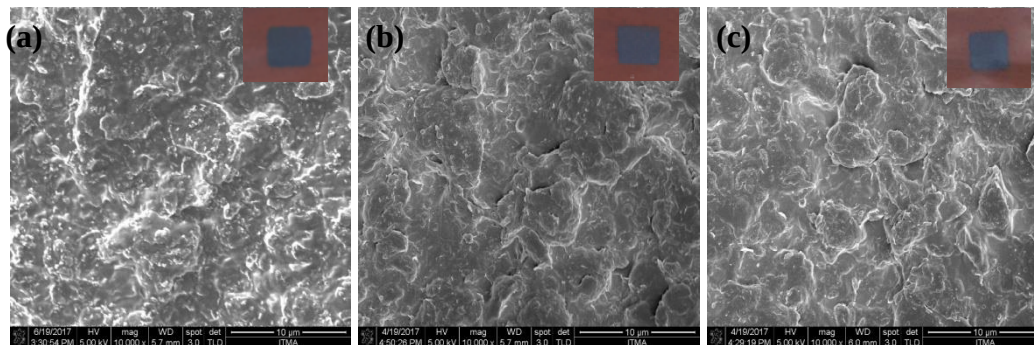


Figure 5: FESEM image of graphite thick film with firing temperature @ 300°C: (a) 1 hour (S1), (b) 2 hours (S2), and (c) 3 hours (S3)

Figure 5 shows the morphology of the thick film with firing temperature fixed at 300°C but with different holding time in the furnace. After 1 hour, small particles are still visible among large grains. When holding time is increased to 2 hours, it can be observed that the particles densified and formed larger grains, although there are still small amount of small particles visible. After 3 hours, almost all particles densified and formed large grains. This proved that longer firing holding time helped the process of densification of the particles, which can give better conductivity of the thick film. Next, the effect of higher firing temperature is studied. Figure 6 shows the morphology of the thick film with firing temperature at 300°C and 400°C, but with same holding time which is 1 hour. As can be observed from the images, when the firing temperature is increased, the densification of particles occurred, creating enlarged grains and leading to better conductivity of the thick film.

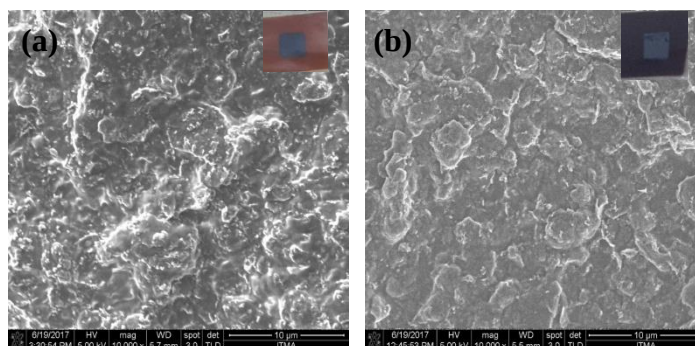


Figure 6: FESEM image of milled graphite powder thick film : (a) firing temperature @ 300°C (S1), (b) firing temperature @ 400°C (S4)

Finally, the sheet resistances for all samples are shown in Table 1. As hypothesized from the morphology of the thick films, samples with longer holding time and higher firing temperature give lower resistance. This means that the resistivity of these samples are lower, resulted in higher conductivity as compared to other samples. Sample with firing temperature of 400°C with holding time of 1 hour has the best results as compared to others. Meanwhile, a comparison is also made with thick film that used unmilled graphite powder. The results showed that by using milled graphite powder which has a combination of micrometer and nanometer sized particles, the conductivity improved significantly. This may due to the existence of smaller particles which resulted in proper densification of the grains, leading to better conductivity of the thick film itself.

Table 1: Sheet resistance of milled graphite powder thick film

Sample	Firing temperature (°C)	Firing holding time (hr)	Sheet resistance (Ω/cm^2)
S1	300	1	46.4
S2	300	2	30.0
S3	300	3	27.2
S4	400	1	10.9
Unmilled graphite thick film	300	1	70.1

CONCLUSION

From the results, it can be concluded that the developed graphite thick film has good conductivity with low firing temperature as compared to current thick films which requires higher firing temperature to achieve good conductivity. Longer holding time and higher firing temperature can further improve the conductivity of the thick film, making it suitable for screen printing onto flexible polymer substrate such as Kapton film. Further work of this project is to study adhesion of the thick film to the film substrate to observe the flexibility of the thick film itself.

ACKNOWLEDGMENT

The author wishes to thank Universiti Putra Malaysia for funding of the project under Geran Putra (GP-I/9439400), and all staffs and students at Institute of Advanced Technology (ITMA) for assistance and support throughout the project.

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