Faculty of Mechanical Engineering

A STUDY ON MECHANICAL AND ELECTRICAL PROPERTIES OF HYBRIDIZED GRAPHENE-CARBON NANOTUBE FILLED CONDUCTIVE INK

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Master of Science in Mechanical Engineering

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MAIZURA BINTI MOKHLIS

A thesis submitted
in fulfillment of requirements for the degree of Master of Science
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2020

DECLARATION

I declare that this thesis entitled "A Study On Mechanical and Electrical Properties Of Hybridized Graphene-Carbon Nanotube Filled Conductive Ink" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : …………..

Name : …………..

Date : …………..

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Mechanical Engineering.

Signature	:	……………...............................
Supervisor Name	:	……………...............................
Date	:	……………...............................

DEDICATION

To my beloved family and friends

ABSTRACT

Many researchers are now competing to fabricate an electronic device to meet the technological demand by using new conductive materials. There are several varieties of conductive inks on the market and it is crucial to choose the right ink fitting in the electronic applications. Conductive ink is a special type of ink that allows an electric current to flow through the ink. The conductive ink-filled epoxy is also known as conductive composites because the ink itself is based on more two ingredients such as filler, binder, and hardener. As interconnect material, the conductive inks should feature good electrical, mechanical and thermal properties. Nonetheless, to-date, there are some issues with current conductive ink that available in the market namely printing quality, high electrical resistivity as well as inferior mechanical strength. Therefore, this study aims to produce highly functional conductive ink using two types of carbon-based conductive fillers with epoxy as a binder. More specifically, graphene nanoplatelets (GNP) and multiwalled carbon nanotube (MWCNT) were used to produce the hybrid conductive ink. As a baseline, both fillers, GNP and MWCNT with epoxy were formulated separately using a minimum percentage at the beginning and the amount of filler was increased based on the conductivity level required. The percentage of filler for GNP was varied from 10-35 wt.% while for MWCNT for by 3-8 wt.%. It is very important to make sure the materials are in contact with each other and therefore the movement of an electron will become easier. Following this, the hybridization of these two materials was made to produce conductive ink with enhanced functionality. The fabrication of the ink was carried out by using a direct mixing method starting from the formulation of the ink, mixing process, printing process and curing process to produce highly conductive hybridized ink. This research also studies the effect of the temperature on electrical, mechanical properties and surface roughness of the hybrid conductive ink using a varying amount of filler for both GNP and MWCNT inks. The electrical properties and the mechanical properties were assessed using a Four-point probe by following the ASTM F390 and a Dynamic Ultra Microhardness using ASTM E2546-15 as a guideline. The experimental results demonstrate an improvement in electrical conductivity. GNP showed higher resistivity around 38 kohm/sq whereas MWCNT showed much lower resistivity around 3.3 kohm/sq. When the hybridization occurs, the result obtained somewhat lower than MWCNT about 2.9 kohm/sq possibly due to the synergistic effect between the GNP and MWCNT, with better distribution and tunneling of electrons between both carbon-based conductive fillers. For mechanical properties, the hardness of hybrid ink is lower hence high in elastic modulus compared to GNP and MWCNT due to local stress concentration in the matrix. Furthermore, the surface roughness of hybrid resulted a smooth surface with the value of 0.833 µm compared to individual fillers. Smooth surface allow continuous conductive line formation without shorting risk.

ABSTRAK

Ramai penyelidik kini bersaing untuk menghasilkan alat elektronik untuk memenuhi permintaan teknologi dengan menggunakan bahan-bahan konduktif baru. Terdapat beberapa jenis dakwat konduktif di pasaran dan adalah penting untuk memilih dakwat yang sesuai dalam aplikasi elektronik. Dakwat konduktif adalah sejenis dakwat yang membolehkan arus elektrik mengalir melalui dakwat. Dakwat konduktif berisi epoxy juga dikenali sebagai komposit konduktif kerana dakwat itu sendiri adalah berasaskan lebih daripada dua bahan seperti pengisi, pengikat, dan pengeras. Sebagai bahan penyambung, dakwat konduktif harus mempunyai sifat elektrik, mekanikal dan haba yang baik. Walau bagaimanapun, setakat ini, terdapat beberapa isu dengan dakwat konduktif semasa iaitu kualiti percetakan, rintangan elektrik yang tinggi serta kekuatan mekanikal yang rendah. Oleh itu, kajian ini bertujuan untuk menghasilkan dakwat konduktif yang sangat berfungsi dengan menggunakan dua jenis pengisi konduktif berasaskan karbon dengan epoksi sebagai pengikat. Lebih khusus lagi, GNP dan MWCNT digunakan untuk menghasilkan dakwat konduktif hibrid. Sebagai garis dasar, kedua-dua pengisi, GNP dan MWCNT dengan epoksi dakwat digubal secara berasingan dengan menggunakan peratusan minimum pada permulaan dan jumlah pengisi telah meningkat berdasarkan tahap kekonduksian yang diperlukan. Peratusan pengisi untuk GNP adalah berbeza – beza bermula daripada 10-35 wt.% manakala untuk MWCNT bermula daripada 3-8 wt.%. Ia adalah sangat penting untuk memastikan bahan-bahan ini berhubung antara satu sama lain dan oleh itu pergerakan elektron akan menjadi lebih mudah. Berikutan itu, penghibridan kedua-dua bahan itu dibuat untuk menghasilkan dakwat konduktif dengan fungsi yang dipertingkatkan. Pembuatan dakwat telah dijalankan dengan menggunakan kaedah pencampuran terus bermula dari penggubalan dakwat, proses pencampuran, proses percetakan, dan proses pengawetan untuk menghasilkan dakwat hibrid yang sangat konduktif. Kajian ini juga mengkaji kesan suhu pada sifat-sifat elektrik, mekanikal dan kekasaran permukaan dakwat konduktif hibrid yang menggunakan jumlah pengisi yang berbeza-beza untuk kedua-dua dakwat GNP dan MWCNT. Sifat-sifat elektrik dan sifat-sifat mekanikal dinilai menggunakan empat titik kuar mengikut F390 ASTM dan dinamik ultra mikro kekerasan menggunakan ASTM E2546-15 sebagai garis panduan. Keputusan eksperimen menunjukkan peningkatan kekonduksian elektrik. GNP menunjukkan kerintangan yang lebih tinggi sekitar 38 kohm/sq manakala MWCNT menunjukkan kerintangan lebih rendah sekitar 3.3 kohm/sq. Apabila penghibridan berlaku, keputusan yang diperolehi agak lebih rendah daripada MWCNT kira-kira 2.9 kohm/sq mungkin disebabkan oleh kesan sinergy antara GNP dan MWCNT, dengan pengagihan yang lebih baik dan terowong elektron antara kedua-dua pengisi konduktif berasaskan karbon. Bagi sifat mekanikal, kekerasan dakwat hibrid adalah lebih rendah tetapi tinggi dalam modulus elastik berbanding GNP dan MWCNT kerana penumpuan tegasan tempatan dalam matriks. Tambahan pula, kekasaran permukaan hibrid menyebabkan permukaan yang licin dengan nilai 0.833 µm berbanding pengisi individu. Permukaan yang licin membolehkan pembentukan garis konduktif berterusan tanpa risiko pintasan.

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Wassalam.

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LIST OF ABBREVIATIONS

1D	-	One dimensional
2D	-	Two dimensional
AA	-	Arithmetic average
Ag	-	Silver
ASTM	-	American society for testing and materials
BPA	-	Bisphenol – A
CIJ	-	Continuos inkjet
CLA	-	Centerline average
CNT	-	Carbon nanotube
CSM	-	Continuous stiffness method
Cu	-	Copper
DLP	-	Digital light process
DOD	-	Drop-on-demand
EDX	-	Energy dispersive x-ray
FPE	-	Flexible printed electronics
GNP	-	Graphene nanoplatelets
HDPE	-	High density polyethylene
MIMIC	-	Micromolding in capillaries
MWCNT	-	Multiwalled carbon nanotube
PCB	-	Printed circuit board

PE	-	Printed electronic
PET	-	Polyethylene Terephthalate
PMMA	-	Polymethyl methacrylate
PVC	-	Polyvinyl chloride
REM	-	Replica molding
RFID	-	Radio-frequency identification
SAMIM	-	Solvent assisted micromolding
SEM	-	Scanning electron microscopy
SWCNT	-	Single wall carbon nanotube
TEM	-	Transmission electron microscopy
Tg	-	Transition temperature
TPU	-	Thermoplastic polyurethane
TRG	-	Thermally reduced graphene
TRGO	-	Thermally reduced graphene oxide
µCP	-	Microcontact printing
µTM	-	Microtransfer molding

LIST OF PUBLICATIONS

The research papers produced and published, awards and conference during the course of this research are as follows:

Journals:

1. Mokhlis, M., Salim, M.A., Masripan, N.A., Md. Saad. A., and Omar, G., 2019. Electrical Performance of Graphene Materials with Different Filler Loading for Future Super Conductor. *Science and Technology Research Institute for Defence (STRIDE)* (Vol. 12, Num. 2). (Published)

2. Mokhlis, M., Salim, M.A., and Masripan, N.A., 2018. Electrical performance of graphene with different filler loading as conductive ink. In *1st Colloquim Paper: Advanced Materials and Mechanical Engineering Research (CAMMER'18)*, 1, pp. 57. Penerbit Universiti, Universiti Teknikal Malaysia Melaka. (Published)

Awards:

1. Silver award in *PECIPTA 2019* for project tiltle 'Graphene-Cnt-Copper ink based on mechanical and electrical behaviour'.

2. Silver award in *International, Invention, Innovation & Technology Exhibition (ITEX2019)* for project title ‘Super conductive graphene nanoparticles ink for printed electronic’.

3. Bronze award in *Jejak Inovasi UTeM 2018* for project tittle ‘Functionality test rig for flexible and stretchable conductive film printed by ink’.

4. Silver award in *Jejak Inovasi UTeM 2018* for project tittle ‘Nanoscale Graphene for future super conductive materials’.

5. Gold award in *EREKA 2018* for project title ‘DIY formulation conductive ink for basic application’.

Conference:

1. Oral speaker in Graphene Malaysia 2019 (MYNANO2019) for project title ‘Graphene as alternative materials for mechanical-electrical conductive filled epoxy’.

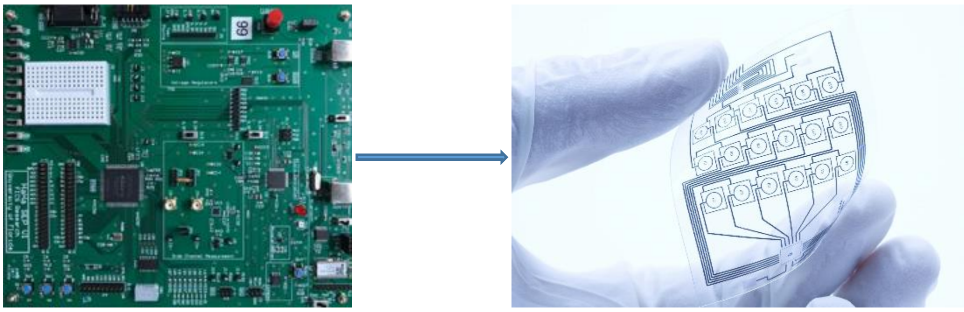
CHAPTER 1

INTRODUCTION

This chapter provides information about conductive ink so that the reader will understand what it is. The crucial information that will determine the flow of this project also included which are background of the study, problem statements, objectives, scope and limitations, potential benefits of the study and outline of the research.

1.1 Background of the research

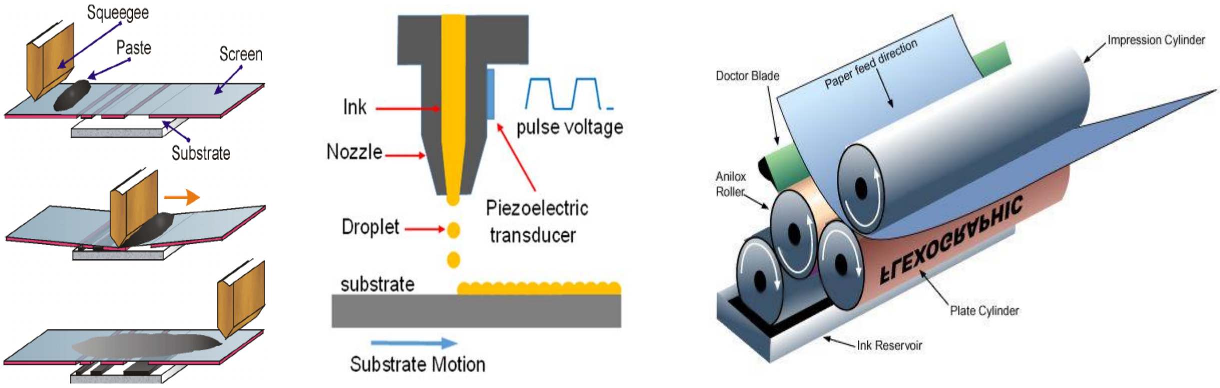
Printed electronics (PE) is an all-encompassing term for the printing method used to create an electronic device by printing on a variety of substrate (Cui, 2016). According to the trend among consumer, further progress in electronic manufacture driving towards emerging research to expand towards thin and flexible electronic. Flexible printed electronics (FPE) combines features of flexible electronics and printed electronics (Wang et. al., 2016; Huang et. al., 2018). Printed electronics (PE) is used to replace the conventional printed circuit board which actually create a drawback in term of cost which is expensive, complex manufacturing process and at the same time it generates the pollutant that can cause harm to the environment compared to printed electronic which far way more affordable to be produced, simple processing and do not harm to the environment. According to the consumer trend, they tend to have miniaturized electronic, therefore the printed electronic can provide more sophisticated electronic in term of lightweight, thin and flexible to the consumer (Khartik et. al., 2015). Figure 1.1 (a) Printed circuit board (PCB) and (b) Flexible substrate show a transformation of electric circuit from conventional to printed electronic.



(a) (b)

Figure 1.1: A diagram of transformation of electric circuit (Bhunia et. al., 2019)

PE was produced through the printing technologies. The concept of printing technologies is to spread and pattern the ink/paste directly on the substrate with the help of specific printing equipment such as screen printing, inkjet printing, and flexography as shown in Figure 1.2 (Dang et. al., 2017). This printing technology is one of the alternatives to substitute conventional technology which is lithography technology.



Screen-printing 3D/Ink jet printing Flexography/Gravure

Figure 1.2: Types of printing technologies (Khan et. al., 2015)

Litography technique is the series of steps that establish the shape, dimension and location of the various components of the integrated circuit. Generally, lithography technology involves several processes which are vacuum processing, chemical deposition, and etching. Figure 1.3 presents the schematic of standard litograhy techniques. However, this lithography technology create the drawback in term of environmental issue as it involves the etching steps which used the corrosive solvent that cause the limitation in substrate choice and at the same time, the lithography technologies itself involve complex process rather than printing technologies (Ramsey et. al., 1997; Sirringhaus et. al., 2000; Calvert, 2001). The main component in printing technologies is conductive ink (Huang et. al., 2019).

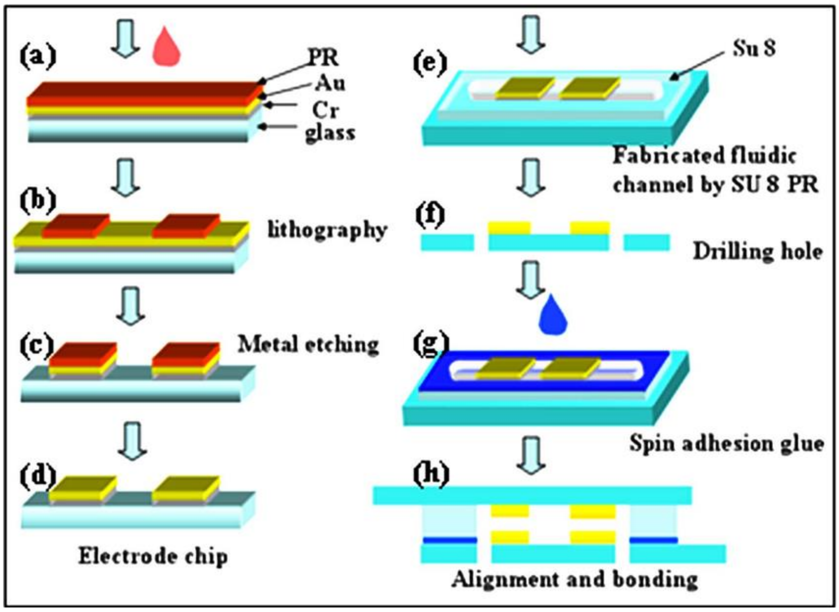


Figure 1.3: Schematic of standard litography techniques for chip fabrication (Cheng et. al., 2007)

Conductive ink is a form of ink that can conduct electricity which the ink infused with a conductive material to enable the electrical conduction and can be printed directly on a substrate or any flexible surface through a regular printing process. The inks are usually applied to the substrate and slightly heated to evaporate the solvent and heat the conductive particles together (Yang et. al., 2016). Conductive ink is a significant component for any application, with widespread uses in wearable electronic (Van den Brand et. al., 2015; Gao