ANALYSIS ON THE MIXING PROCESS AND THE SUBSTRATE SURFACE TREATMENT OF THE STRETCHABLE CONDUCTIVE INK

NUR ARIFAH BINTI MOHD YUSOFF

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

ANALYSIS ON THE MIXING PROCESS AND THE SUBSTRATE SURFACE TREATMENT OF THE STRETCHABLE CONDUCTIVE INK

NUR ARIFAH BINTI MOHD YUSOFF

A report submitted

In fulfillment of the requirement for the degree of

Bachelor Mechanical Engineering (Structure and Materials)

Faculty of Mechanical Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2022

DECLARATION

I declare that this project entitled “Analysis on The Mixing Process and The Substrate Surface Treatment of The Stretchable Conductive Ink” is the result of my own work except as cited in the references.

Signature : ……………………………………………

Name : ……………………………………………

Date : ……………………………………………

APPROVAL

I hereby declare that I have read this project report and in my opinion this report is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering (Structure and Materials)

Signature : ……………………………………….

Name : ……………………………………….

Date : ……………………………………….

DEDICATION

To my beloved

Noor Aziha Binti Bakar and Mohd Yusoff Bin Basir

ABSTRACT

This research demonstrates the optimized mixing parameters of stretchable conductive on the sheet resistivity performance and the effect of chemical surface treatment on the substrate of the stretchable conductive ink. The mixing parameter was divided into three ranges which are 400 rpm in 10 minutes, 1500 rpm in 30 minutes, and 2000 rpm in 60 minutes. A rectangular shape of TPU is used as the substrate in this experiment. The mixture of ink consists of GNPS as a filler, PEDOT:PSS as a functional binder, and a few types of solvents used such as DMSO, EG, and Triton X-100. Sheet resistivity performance measured for all samples shows that the best mixing parameter is 400 rpm in 10 minutes reached the lowest sheet resistivity compared to another sample. Two types of adhesion promoters were used in this experiment as chemical surface treatment such as Methyl Ethyl Ketone (MEK) and Anchor Spray Paint (ASP). The adhesion promoter was applied on the TPU substrate before printing the conductive ink. Then, the sheet resistivity performance was measured on the sample and plot the comparison with the sample without adhesion promoter. Thus, it can be concluded that the sample with adhesion promoter reached the lowest sheet resistivity performance.

ABSTRAK

Penyelidikan ini menunjukkan parameter pencampuran yang dioptimumkan bagi konduktif boleh renggang pada prestasi kerintangan kepingan dan kesan rawatan permukaan kimia pada substrat dakwat konduktif boleh renggang. Parameter pencampuran dibahagikan kepada tiga julat iaitu 400 rpm pada masa 10 minit, 1500 rpm pada masa 30 minit, dan 2000 rpm pada masa 60 minit. TPU yang berbentuk segi empat tepat digunakan sebagai substrat dalam eksperimen ini. Campuran dakwat terdiri daripada GNPS sebagai pengisi, PEDOT:PSS sebagai pengikat berfungsi, dan beberapa jenis pelarut yang digunakan seperti DMSO, EG, dan Triton X-100. Prestasi kerintangan kepingan yang diukur untuk semua sampel menunjukkan bahawa parameter pencampuran terbaik ialah 400 rpm pada masa 10 minit mencapai kerintangan kepingan terendah berbanding dengan sampel yang lain. Dua jenis promoter lekatan digunakan dalam eksperimen ini sebagai rawatan permukaan kimia seperti Methyl Ethyl Ketone (MEK) dan Anchor Spray Paint (ASP). Penganjur lekatan telah digunakan pada substrat TPU sebelum mencetak dakwat konduktif. Kemudian, prestasi kerintangan kepingan diukur pada sampel dan plotkan perbandingan dengan sampel tanpa promoter lekatan. Oleh itu, boleh disimpulkan bahawa sampel dengan promoter lekatan mencapai prestasi kerintangan kepingan terendah.

ACKNOWLEDGEMENT

I would like to express my gratitude to Allah SWT for giving me an opportunity to participate and able to complete this Projek Sarjana Muda (PSM) report and prepared a few sample of experiments on time in order to fulfill the requirement of PSM criteria

On the other hand, I sincerely dedicate my gratitude to everyone who assisted and guided me in completing my PSM journey especially Dr Mizah Binti Ramli as my great supervisor. She keep on giving motivations, advices and guidance to carry out my study and experiment in Analysis on The Mixing Process and The Substrate Surface Treatment of The Stretchable Conductive Ink.

Besides that, a big thank you to all the team members that always give a hand and willing to sacrifice their time to help me. Also, to all my lectures in Universiti Teknikal Malaysia Melaka; specifically, FKM in which without their knowledge sharing, I wouldn't be able to complete the experimental procedure and technical report writing.

Support from my parents and my close friend are one of my strength to finish my PSM journey.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

This chapter consists of the project background, problem statement, objectives, the scope of the project, and the general methodology of the Analysis on The Mixing Process and The Substrate Surface Treatment of The Stretchable Conductive Ink.

1.1 Background of Study

The research to complete this project was generally to study the process of a simple mixture of the ink to validate the optimized mixing parameter of stretchable conductive ink on the sheet resistivity performance and to investigate the effect of chemical surface treatment on the substrate of the stretchable conductive ink. The stretchable conductive ink is one of the effective material which allows the ink film to undergo better electrical conductivity after applied any forces into it such as stretching or folding. It has wide application possibilities in the branch of learning flexible electronic devices.

There are a few applications that can gain from this technology including neuro-prosthetics, flexible displays, soft robotics, cardio-stimulating implants, and other curvilinear systems such as an aircraft wing. A mixture of metallic particles with a solvent is described a conductive ink. The ink normally involves three different groups of materials. Metallic powders like Ag, Au, or Cu are labeled as the first group. It may include nano-materials to enhance sintering and low- temperature melting of the listed conductive powders.

A polymers binder is categorized in the second group which plays the greatest role in combining the metallic powders to the substrate during and after the sintering process. The third group generally includes non-volatile organic polymers and volatile solvents which bring about the rheological properties for screen printing. It will act as a transporter for the metallic powders and together with polymers binder during the sintering process and screening process. The binder performed an essential role in assist the ink to adhere to the substrate by contributing stretch-ability at the sintered state. The requirement of the stretchable conductive ink is it able to stretch after completing the sintering procedure and still keep up the ohmic connectivity between the metal flakes.

A flexible substrate such as polydimethylsiloxane (PDMS) and Thermoplastic Polyurethane (TPU), a listed metallic powders including Ag-PDMS and elastic components which are LED, transistor, resistor, capacitor, and integrated circuit mainly a part of a stretchable conductive circuit. Elastomers, TPU and PDMS are often used as substrates in numerous electronic devices and flexibly stand high deformations that bigger than 200% strain. This procedure shows the high electrical resistivity of the devices.

1.2 Problem Statement

There are several articles mentioned about the conductive filler that had been experimentally tested and used as a new engineering technology which is the most popular one is silver. However, based on the current literature review, they are considering the price range of the materials and some factors regarding mass production for widely used in electronic capsulation in the future. On the other hand, silver material is quite pricey and limited compared to graphene which saves costs with excellent environment stability and had the highest thermal conductivity among them, along with special properties suitable for range of applications. Graphene Nanoplatelets (GNPs) had been chosen in this project because of an effective reinforcement shown in polymer materials. GNPs were established to have uncomplicated process-ability with the added advantage of improving practical and biological properties of the composites. Plus, there also limited knowledge about the optimized results of the designed experiment such as the best mixing speed, and mixing time for the graphene materials and the effect of chemical surface treatment on the substrate of the stretchable conductive ink.

1.3 Objectives

The objectives of this project are listed below:

i. To optimize the mixing parameters of stretchable conductive ink on the sheet resistivity performance.

ii. To investigate the effect of chemical surface treatment on the substrate of the stretchable conductive ink.

1.4 Scope of the Project

The making of graphene is by "unzipping" the carbon nanotubes. Both of them have exceptional mechanical and electronic properties. Graphene is listed as one of the strongest materials that have superior properties and optical properties, good tensile strength, and excellent electrical conductivity. This project covered on an Analysis on The Mixing Process and The Substrate Surface Treatment of The Stretchable Conductive Ink. The optimized mixing parameters regarding on suitable mixing time and mixing speed will measured based on sheet resistivity performance of each samples. This experiment also considered the process of testing the chemical surface treatment by applying an adhesion promoter at the TPU substrate to measure the sheet resistivity performance and make a comparison with a samples without adhesion promoter. The adhesion promoter will only apply for the samples that have achieved the best mixing parameters which shows the lowest sheet resistivity. Two different adhesion promoter used as chemical surface treatment in this experiment including Methyl Ethyl Ketone (MEK) and Anchor Spray Paint. Adhesion promoter can rise up the adhesion by incorporating functional additives into the adhesive formulation that produce chemically bond to the substrate. It definitely will improve the initial joint strength and prevent delamination of the adhesive from the substrate.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Regarding this chapter, literature reviews conducted encompassed Thermoplastic Polyurethane (TPU) substrate, conductive ink, a solvents used, mechanical testing method, and adhesion promoter for chemical surface treatment. The main point is included substrates, ink, solvents used, and printing techniques, mechanical testing and adhesion promoter with detailed descriptions on each point.

2.2 Flexible Electronics

Technology in electronic circuits is majorly used a flexible electronics and has been around for several decades. Anything thin or long can become flexible. To fabricate a flexible device in an uncomplicated and efficient manner, manufacturing technologies should be readily accessible, inexpensive, and most importantly are ready to use. It is usually connected with pattern transfer, solution printing processes, additive manufacturing technologies, and roll-to-roll capabilities. Plus, the flexible circuit can be printed by using a spot of conductive ink.

Transfer and bonding of finalized circuits to a flexible substrate and fabrication of the circuit straight on the flexible substrate are the two basic approaches that have been employed to make flexible electronics. The whole transfer is fabricated by standard methods on a carrier substrate like a Si wafer on a glass plate in the transfer-and-bond approach. It advances over the original flexible wafer-based solar cell arrays. Their drawbacks are slight surface area coverage and expensive. In various applications, most of the surface will be covered with electronics fabricated straight on the substrate. There a few approaches to integrating disparate materials and oftentimes flexible substrates are not fit with the existing planar silicon microfabrication process.

To increase the power and weight ratio from the history of the flexible circuit, any kind of item thinned becomes flexible cause the silicon solar cell becomes thinner to approximately 100 µm. The thinned solar cells then were assembled on the plastic substrate to reach flexibility forty years ago. It can be classified into three different categories in terms of mechanical characteristics for flexibility which are (a) Rollable or bendable. (b) Elastically shaped and (c) permanently shaped. All the categories can be shown in Figure 2.1 below.

(a) (b)

(c)

Figure 2. 1: (a) Bendable Circuit (b) Silicon island on spherically shaped foil substrate (c) Concept of conformably shaped digital dashboard (Sarma, 2009)

The used electrical connections classify as one of the most advanced and important technologies because of their beneficial properties such as marginal weight, thinness factor, and flexibility. It will help in improving the device functionality by coming up with portability function, freedom form or flexible, resistance impact, reduce the product weight and thickness.

2.3 Conductive Ink

Conductive inks made of dispersed metallic, carbon, or conductive polymer nanoparticles have been prepared and placed on a low-cost substrate for radio frequency identification (RFID) capacitive coupled antennas. It is the most important component in the printing of metallic structures. A few conductive materials could be listed for this purpose such as conductive polymers, carbon, organic or metallic compounds, metal NPs and metal precursors. Most of the conductive inks are referred to as metal NPs. The reason that can be concluded from that is regarding their resistivity is near to that of bulk materials (2-3 times higher) as opposed to conductive materials whose resistivity is higher.

The metallization using NPs inks requires the following two steps in a row: printing of the inks and sintering to convert the inks into a conductive, solid metal track. For now, the major approach for printing metals is based on metal ink formulation, which can be printed and then sintered to acquire a metallic layer. Metal inks and pastes were grown for printing methods used in the graphics arts industry such as screen printing, flexography, inkjet printing, offset, and gravure.

To make sure a good conductivity, the ink needs to dry at room temperature or using cure techniques by cure the ink in the oven on a certain curing time to shift the solvents to strengthen the connections between metal particles. After the drying process is completed, the solvents will be removed by the evaporation process. Silver-based ink particles reach a conductivity of approximately 10^5 S/m compared to bulk copper is 59 x 10^7 S/m, unfortunately, this conductivity can be upgraded with an optimized annealing step. Organic inks based on graphene [HUA 11] and carbon nanotubes [DEN 09] are valid but the production is small with conductivities of approximately $10^2 – 10^3$ S/m. this guide to the considerable increase in losses by conduction in the conductive materials (Vena et al, 2016).

Conductive ink can be separated into two types which is particle and non-particle where also can be categorized into organic and non-organic because the solvent used a different ink (Khirotdin et al., 2016). Electrical properties that utilize a different kind of carbon because of a complex arrangement and interact between the morphology and size of the parts initiate properties, and the control techniques used to scatter them.

2.3.1 Carbon Ink

The type of ink highlighted in this project is carbon-based ink or graphene. Graphene is categorized as the mother of all graphitic forms of carbon. This is the basic structure of all carbon allotropes. Carbon atoms are uniformly arranged in a hexagonal lattice and tightly packed by sp2 hybrid bonds which is a one atom thick carbon layer (0.345 Nm thick). In 2014, Andre Geim and Kostya Novoselov isolated that this is the thinnest and world's first 2D material (Iqbal et al., 2020). The structure of graphene owns numerous fascinating properties such as good mechanical strength with Young's modulus of 1 Tpa and ultimate tensile strength of 130 Gpa, high stiffness, and extremely high thermal conductivity up to 5000 Wm-1K-1 plus elevated specific surface area.

Normally, graphene avoids to use in unalloyed form because of its insufficient yield rather than graphene derivatives such as graphene oxide (GO), reduced graphene oxide (rGO), and functionalized reduced graphene oxide (frGO) are being used universally as they exhibit similar properties of graphene. Consequently, the requirement of graphene materials over the past few years has been increased to cover the demand in both industry and academia for commercial applications and research.

2.4 Dimethyl Sulfoxide (DMSO)

Dimethyl Sulfoxide (DMSO) classified as organosulfur compound with the formula $(CH_3)_2SO$. It is a colourless liquid that important polar aprotic solvent that dissolves bothpolar and non-polar compounds in a wide range of organic solvent as well as water. It was first Russian scientist Alexander Zaytsev who reported his findings in 1867. DMSO is undustrially produced from dimethyl sulfide, a by-product of the Kraft process, by oxidation with oxygenor nitrogen dioxide. The kraft process known as kraft pulping or sulfate process is a method for conversion of wood into wood pulp, which consists of all pure cellulose fibers, the main component of paper. DMSO evaporates slowly at normal atmospheric pressure because of its high boiling point, 189 °C (372 °F) while the high freezing point of DMSO, 18.5 °C (65.3 °F). Samples mixed with DMSO cannot be easily recuperated compared to other solvents, as it is very hard to erase all traces of DMSO by conventional rotary evaporation. DMSO also can be used as *in vitro* and *in vivo* drug testing, biology, medicine, alternative medicine, veterinary medicine and taste. DMSO used as the primary solvent that exhibits good conductivity and low baseline resistance at room temperature (Seekaew et al., 2014).

2.5 Triton X-100

It is a nonionic surfactants that has a hydrophilic polyethylene oxide chain and comes with aromatic hydrocarbon lilophilic or hydrophobic group. Triton X-100 was registered trademark of Rohm & Haas Co. Undiluted Triton X-100 is a clear viscous fluid which have less viscous than undiluted glycerol which produced a viscosity about 270 centipoise at 25 °C which comes down to about 80 centipoise at 50 °C. It is soluble in water at 25 °C, toluene, xylene, trichloroethylene, ethylene glycol, ethyl ether, ethyl alcohol, isopropyl alcohol and ethylene dichloride while insoluble in kerosene, mineral spirits and naphtha unless a coupling agent like oleic acid is used.

In common, Triton X-100 used in detergent in laboratories and widely used to lyse cells to extract protein organelles, or to pemeabilize the membranes of living cells. J. -B. Raoof eta al. [82] studied the effect of TX-100 film on the carbon (carbon nanotube) paste electrodes for detecting formaldehyde. They found that, TX-100 increases the electrocatalytic activities of the carbon surfaces by increasing its active surface area for the formaldehyde redox reactions. B. E. K. Swamy et al. [35, 77, 79, 83] modified the carbon (graphite) paste electrodes by TX-100 for sensor applications. They 135 found that, TX-100 increases the voltammetric signals of the carbon electrode sensors by increasing graphite active surface area. S. Ghasemi and F. Ahmadi [84] has proved the effect of TX-100 on the charge transfer properties of graphene. They found that charge transfer properties of graphene were improved by TX-100 (Jayaprakash & Flores-Moreno, 2017).

2.6 Ethylene Glycol (EG)

It is an organic compound with the formula of (CH2OH)$_2$ is mainly used as a raw material in the manufacture of polyester fibers and for antifreeze formulation. Ethylene Glycol is a colorless, an odorless, toxic, sweet-tasting and viscous fluid. Ethylene Glycol is produced via intermediate ethylene oxide form ethylene (ethane). Ethylene glycol will produced according to the chemical equation after ethylene oxide is react with water. Acidic occur when ethylene glycol reach the highest yield or neutral pH with a large excess of water.

Ethylene Glycol is an important precursor to polyester fibers and resin in the plastic industry. A popular and promising strategy has been the functionalization with poly (ethylene glycol) (PEG-GO) through covalent bonding or non-covalent interactions, which imparts remarkably high aqueous stability as well as enhanced biocompatibility (Ghosh & Chatterjee, 2020). EG and triton x-100 were added to improve of the viscosity and surface tension as well as to prevent of rapid drying and clogging in the printer head (Seekaew et al., 2014).

2.7 Poly(3,4-Ethylenedioxythiophene) Polystyrene Sulfonate (PEDOT:PSS)

PEDOT:PSS is a polymer mixture of two ionomers. Polymer known as substance or material that consisting very large molecules, or macromolecules, composed of various repeating subunits. Both synthetic and natural polymers play essential roles in everyday life due to their spectrum of properties. PEDOT is a conjugated polymer and carries positive charges and is based on polythiophene. Polythiopenes or PTs are polymerized thiopenes, a sulfur heterocycle. PEDOT:PSS can be served by mixing an aqueous solution of PSS with EDOT monomer and to the resulting mixture, a solution of sodium persulfate and ferric sulfate.

It has the largest efficiency among conductive organic thermoelectric materials and can be used in flexible and biodegradable thermoelectric generators. The conductivity of PEDOT:PSS can be improved by a post-treatment with various compound such as dimethyl sulfoxidde (DMSO), ethylene glycol (EG), salts, cosolvents, acids, alcohols, phenol and amphilic fluoro-compounds. A water-based inks of PEDOT:PSS generally used in slot die coating, flexography, rotogravure and inkjet printing. It has a lower electrical mobility than silicon which can incorporated into flexible electronics.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a conjugated polymer (a mixture of two ionomers) widely used as the active material in flexible and printed electronics because of its good electrical conductivity, high transparency, low redox potential and good processability. However, its limited structural and chemical properties remain major obstacles that inhibit its use in various practical applications (Seekaew et al., 2014).

2.8 Substrate

There are various substrate that useful as each of the substrate owns their surface resistivity. The substrate that commonly used for a research purposes are Polyethylene Terephthalate (PET), Polypropylene (PP), Polyvinyl Chloride (PVC), Thermoplastic Polyurethane (TPU), and some other more. Polyethylene Terephthalate (PET) and Thermoplastic Polyurethane (TPU) are chosen