ADHESION CHARACTERIZATION OF ELECTRICALLY CONDUCTIVE POLYMER

KO KAR CHOON

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

© Universiti Teknikal Malaysia Melaka

ADHESION CHARACTERIZATION OF ELECTRICALLY CONDUCTIVE POLYMER

KO KAR CHOON

A report submitted
in fulfilment of the requirement for the degree of
Bachelor of Mechanical Engineering (Hons)

Faculty of Mechanical Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2019

© Universiti Teknikal Malaysia Melaka

DECLARATION

I declare that this project entitled "Adhesion Characterization of Electrically Conductive Polymer" is the result of my own work except as cited in the references.

Signature : ……………………………………..

Name : ……………………………..…………

Date : ………………………….……………

© Universiti Teknikal Malaysia Melaka

APPROVAL

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

Signature	: …………………………………
Name of supervisor	: …………………………………
Date	: …………………………………

© Universiti Teknikal Malaysia Melaka

DEDICATION

This project work is dedicated to my beloved family and friends for always been there to support and inspire me throughout my life.

© Universiti Teknikal Malaysia Melaka

ABSTRACT

Electrically conductive adhesive (ECA) had been widely used in various industry especially in the printed electronic industry. Generally, ECAs are mixtures of polymer binder and conductive filler and is an alternative way of replacing the conventional soldering method. ECAs offer more advantages such as lower curing temperature, lead-free, non-lethal, minimal increase in weight of assembly and compatibility with range of substrates. However, one of the challenges faced in conductive ink is the lack of adhesion to the adherend such that the nature of adherent surface influence the adhesive strength. Moreover, the effect of various thickness on the mechanical properties of conductive ink coated on a flexible material still have a lot of open question. This research describes about the adhesion characterization of electrically conductive polymer. The aim of this research is to investigate the mechanical properties of electrically conductive polymer on flexible materials by nanoindentation and to investigate the strength of joints bonded with two layers of different conductive polymers. The methodology used in this research includes the fabrication of specimens, tensile test joints under ASTM D1002 and nanoindentation testing to obtain the mechanical properties of thin film. The results showed that the joints treated with Methyl Ethyl Ketone (MEK) has higher failure load for both single and double layer of conductive polymer. Besides, specimen which was cured with MEK showed lower electrical resistivity due to functional group in MEK influence the electrical conductivity of ECA. As the thickness of the specimen increase, the electrical conductivity also increases. Based on the nanoindentation testing, it is found that the hardness of the film is independent with the thickness of the film. However, the elastic modulus of the film showed an obvious increment as the thickness of the coating increase. Moreover, the creep testing result also showed that the dwell time did not influence the hardness and elastic modulus of the film regarding the different of thickness and dwell time. For future work, it is recommended that the mechanical properties can be further evaluated by using other parameter setting such as constantly increasing the applied load and loading rate for the nanoindentation testing. Besides, it is recommended to use another type of conductive ink such as graphene ink to evaluate the mechanical properties as it is another type of conductive polymer which had been widely used in printed electronic industry.

© Universiti Teknikal Malaysia Melaka

ABSTRAK

Pelekat konduktif elektrik (ECA) telah digunakan secara meluas dalam pelbagai industri terutamanya dalam industri elektronik bercetak. Secara umum, ECA adalah campuran pengikat polimer dan pengisi konduktif dan merupakan salah satu cara alternatif untuk menggantikan kaedah pematerian yang konvensional. ECA menawarkan lebih banyak kelebihan seperti suhu rawatan yang rendah, bebas plumbum, kurang berbahaya, peningkatan berat yang minimum dan keserasian dengan pelbagai substrat. Walau bagaimanapun, salah satu cabaran yang dihadapi oleh dakwat konduktif adalah kekurangan adhesi disebabkan oleh sifat permukaan adhesi mempengaruhi kekuatan pelekat adhesi. Selain itu, kesan pelbagai ketebalan terhadap sifat mekanikal dakwat konduktif yang bersalut pada bahan yang fleksibel masih mempunyai banyak persoalan terbuka. Kajian ini menerangkan tentang pencirian perekatan polimer konduktif elektrik. Tujuan penyelidikan ini adalah untuk mengkaji sifat mekanik polimer konduktif elektrik pada bahan fleksibel dengan nanoindentasi dan untuk mengkaji kekuatan pelekat yang melekatkan dua lapisan polimer konduktif yang berbeza. Metodologi yang digunakan dalam penyelidikan ini termasuk pembuatan spesimen, sendi ujian tegangan di bawah ASTM D1002 dan ujian nanoindentation untuk mendapatkan sifat mekanikal filem nipis. Keputusan menunjukkan bahawa sendi yang dirawat dengan Methyl Ethyl Ketone (MEK) mempunyai beban kegagalan yang lebih tinggi untuk kedua-dua lapisan polimer konduktif tunggal dan dua. Selain itu, spesimen yang telah disalut dengan MEK menunjukkan daya tahan elektrik yang lebih rendah kerana kumpulan fungsional di MEK mempengaruhi kekonduksian elektrik ECA. Apabila ketebalan spesimen meningkat, kekonduksian elektrik juga meningkat. Berdasarkan ujian nanoindentation, didapati kekerasan filem itu adalah tidak dipengaruhi oleh ketebalan filem. Walau bagaimanapun, modulus elastik filem ini menunjukkan peningkatan yang ketara apabila ketebalan lapisan salutan meningkat. Selain itu, hasil uji rayapan juga menunjukkan bahawa masa rayapan tidak mempengaruhi kekerasan dan modulus elastik filem apabila masa rayapan meningkat. Bagi kerja masa depan, adalah disyorkan bahawa sifat-sifat mekanikal boleh dikaji dengan lebih lanjut dengan menggunakan tetapan parameter yang lain seperti meningkatkan beban dan kadar beban yang digunakan untuk ujian nanoindentation. Di samping itu, disyorkan untuk menggunakan jenis lain dakwat konduktif seperti dakwat graphene untuk menilai sifat-sifat mekanik kerana ia adalah satu lagi jenis polimer konduktif yang telah digunakan secara meluas dalam industri elektronik bercetak.

.

© Universiti Teknikal Malaysia Melaka

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my gratitude and thanks to my final year project supervisor, Dr. Mizah Binti Ramli, for her guidance and support by offering me countless of valuable knowledge and suggestion throughout my research.

I would also like to thank to all the technician in Mechanical Engineering Faculty, who help and guide me in the usage of the machine and necessary materials to complete my research. I also wish to thank to Intan Fatihah Binti Ahmad, Doctor of Philosophy from the Faculty of Mechanical Engineering for her help in nanoindentation testing. Most importantly, I extend my gratitude to UTeM for short term financial support throughout this project. Moreover, I also thanks my friends who gave me suggestion and support of encouragement throughout my research. Special thanks

I would also like to express my gratitude towards the panels for their comment and tips which help me to improve my report writing. Last but not least, I would like to express my sincere gratitude and thanks also to all the parties involves either directly or indirectly.

© Universiti Teknikal Malaysia Melaka

TABLE OF CONTENTS

© Universiti Teknikal Malaysia Melaka

© Universiti Teknikal Malaysia Melaka

LIST OF TABLES

© Universiti Teknikal Malaysia Melaka

LIST OF FIGURES

© Universiti Teknikal Malaysia Melaka

© Universiti Teknikal Malaysia Melaka

LIST OF ABBREVIATIONS

ACA	Anisotropic Conductive Adhesives
ASTM	American Society For Testing and Material
CNT	Carbon NanoTubes
ECA	Electrically Conductive Adhesive
ECP	Extrinsically Conductive Polymer
ICA	Isotropic Conductive Adhesive
ICP	Intrinsically Conductive Polymers
MEK	Methyl Ethyl Ketone
MWNT	Multi-Walled Carbon NanoTube
RFID	Radio Frequency Identification
RTV	Room-Temperature-Vulcanizing
SLJ	Single Lap Joints
SWNT	Single-Walled NanoTube
UTM	Universal Material Testing

© Universiti Teknikal Malaysia Melaka

LIST OF SYMBOLS

%	-	Percentage
wt%	-	Wet percentage
°c	-	Degree Celsius
$cm^2\ Vs^{-1}$,	-	Electron mobiilty
TPa	-	Tera Pascal
Mpa	-	Mega Pascal
T_g	-	Glass transition temperature
P	-	Load
H		Hardness
A		Area
$wm{-}1k{-}1$		Thermal conductivity
S		Stiffness
E_r		Reduced modulus
h		Penetration depth
v	-	Poisson's ratio
cP	-	Viscosity
cm	-	centimeter
mm	-	Milimeter
µm	-	Micrometer
V	-	voltage
I	-	Current
R	-	Resistance
Ω/sq	-	sheet resistance
t	-	thickness
τ	-	Shear stress
g/ml	-	Density

© Universiti Teknikal Malaysia Melaka

CHAPTER 1

INTRODUCTION

1.1 Background

Conducting polymer had been sorted into the two following categories: intrinsically conductive polymers (ICP) and extrinsically conductive polymer (ECP). ICP conducts electricity due to the junction in the backbone polymer which responsible in bringing forth and running charges. The conductivity of ECP is due to the addition of conductive ingredients externally (Vemeker *et al.*, 1960). These type of conducting polymers have numerous advantages compared to metallic conductor such as lighter weight, resistance to electromagnetic, better electrical and mechanical properties (Awuzie, 2017). Compare to metal materials, conductive polymer can be used as a coating onto a substrate at any size and shape.

Conducting polymer had been widely used in other application such as in conductive ink. Conductive ink had been a promising alternative way in print on flexible and wearable electronic device due to their advantages. There is various type of conductive ink which can be printed on flexible circuits. Metal-based ink, conductive polymers and carbon nanomaterials are the three common category types. Nevertheless, each case of conductive ink has their own pros and cons such as high-cost, oxidation issues, high sintering temperature issue and environmental risk (Tran, Dutta and Choudhury, 2018).

© Universiti Teknikal Malaysia Melaka

In electronic packaging manufacturing, electrically conductive adhesives (ECA) which are lead-free had been widely used and started to substitute the conventional soldering method. Many countries are rapidly eliminating the leaded solders in electronic manufacturing. ECAs have lower processing temperature than typical eutectic and lead-free metal solders which is around 100-150°C (Wong, 2004). Besides, ECAs have a range of advantages than compared to other bonding method. Generally, the most important advantages are the possibility of different materials joined together and have a low thermal effect on temperature sensitive materials without damaging it (Kozuh, Kralj and Cvirn, 1997).

1.2 Problem statement

Although the conductive ink has carrier mobility to conduct electricity, there are some challenges that needed to be overcome for further development in future. One of the challenges in conductive ink is the lack of adhesion to the adherend (Tran, Dutta and Choudhury, 2018). The nature of adherent surface influence the adhesive strength during the bonding process between the adhesive and the adherent at contact interface. Thus, surface preparation using chemical treatment can obtain better bond strength.

The demand usage of polymer thin film as an integral component of flexible devises has been increasing throughout the decade. As the size of the polymer thin film of flexible devises continue to diminish, the accuracy for the determination of mechanical characterization of thin film become more important. However, there is still a lot of unknown answer affecting the mechanical properties of thin film as the thickness of polymer film varies (Wang and Feng, 2002).

© Universiti Teknikal Malaysia Melaka

1.3 Objective

The objectives of this project are

I. To investigate the mechanical properties of electrically conductive polymer on PET thin film by nanoindentation.
II. To investigate the strength of joints bonded with two layers of different conductive polymers.

1.4 Scope of project

The scopes covered in this project are as stated below

I. Fabrication of printed circuit using electrically conductive ink.
II. Mechanical characterization of printed circuit on flexible material using nanoindentation and creep testing.
III. Resistivity testing using four-point probe equipment.
IV. Mechanical characterization of joints bonded with two layers of different conductive polymers.

© Universiti Teknikal Malaysia Melaka

CHAPTER 2

LITERATURE REVIEW

Introduction

The review of any related topic about electrically conductive polymer which includes conductive ink, conductive adhesive, printing techniques, mechanical and electrical properties, surface morphology from the previous studies are presented.

2.1 Electrically conductive polymer

A polymer is a material made up of a structure comprises of long, repeating chain molecules. Typically, polymers are a highly resistant material and are often used as an insulator. However, researchers have found that conjugated polymers exhibit electric conductivity behaviour due to the delocalized π electrons along the polymeric backbone (Ramakrishnan, 2011). The electrical conductivity can be further enhanced by the synthesis process called doping, which involve of adding varying amounts from 1% to 30% of oxidising or reducing dopants (*Electrically conductive polymers*, 1991). Conducting polymers such as polyacetylene(PA), polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), Poly(ethylenedioxythiophene) (PEDOT) and etc. have been extensively investigated (Khatoon and Ahmad, 2017). Each conducting polymer is doped with different dopant ion and thus influencing their conductivities as shown in Table 2.1.

© Universiti Teknikal Malaysia Melaka

Table 2.1: Various conducting polymers, dopant ions and their conductivities (Iqbal and Ahmad, 2018)

S.No.	Conducting polymers	Dopant ions	Conductivity (S/cm)
1.	Polyacetylene	I_2, Br_2Li, Na, AsF_5	$10–10^4$
2.	Polyaniline	HCl, $HClO_4$, Camphor	$10^{-1}–2 \times 10^2$
3.	Polythiophene	$FeCl_4^-$, BF_4^-, ClO_4^-, tosylate	10^3
4.	Polypyrolle	BF_4^-, ClO_4^-, tosylate	$500–7.5 \times 10^3$
5.	Poly(p-phenylene)	Li, K, AsF_5	$10^{-1}–10^3$
6.	Poly(p-phenylenevinylene)	AsF_5	10^4
7.	Polyfuran	$BF4^-$, ClO_4^-	100
8.	Polycarbazole	PTSA, $FeCl_4^-$	1.5×10^{-5}

However, the non-conjugated polymer can conduct electricity without affecting its polymeric characteristics by imparting conductive fillers such as carbon black, metallic particles and nanosized conductive particles such as carbon nanotube and graphene (Untereker *et al.*, 2009). These conductive filler form a conductive path within the polymer matrix and causing it to exhibit electrical conductivity behaviour (Brigandi, Cogen and Pearson, 2014). The concentration of the filler used affect the electrical conductivity of a polymer. Based on the percolation threshold theory, the percolation zone as shown in Figure 2.1 is the area where the electrical conductivity increases tremendously with the small usage of filler loading. At the certain level of filler loading, the electric conductivity approaches to the filler materials which is accordingly to the percolation theory (Gurunathan *et al.*, 2013).

© Universiti Teknikal Malaysia Melaka

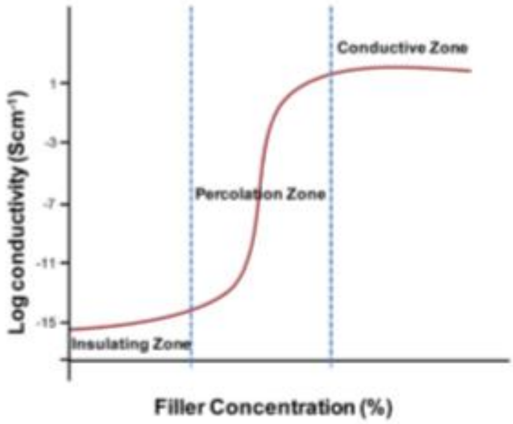

Figure 2.1: Conductivity of polymer composites as function of filler concentration (Kaur *et al.*, 2015)

2.2 Electrically conductive ink

In the process of manufacturing flexible electronic, the conductive circuit is printed onto a thin film substrate. Generally, a layer of conducting adhesive is applied on the surface of the substrate to ensure the adhesion is strong to adhere the conductive ink which is printed by using screen printing or inkjet printing (Brian F. Conaghan *et al.*, 2015). Conductive ink consists of a resin and conductive elements which help to improve its properties such as mechanical strength (Yue Xiao, Belle Mead, 2001). It is preferable that the conductive inks are stable and have low viscosity to prevent aggregation and sedimentation in a solvent (Titkov *et al.*, 2015). There are several types of conductive ink available in the market such as metal and non-metal based ink.

In the preparation of metal-based ink, the metal loading used should be in the range of 20-80wt% (Nir *et al.*, 2009). Among the metal nanoparticles, which have been studied, silver, gold and copper are the ideal materials for the preparation of conductive ink due to their good electrical conductivity and temperature operability. Silver is the most promising material as it is difficult to be oxidised in room temperature (Wang *et al.*, 2017). However,

© Universiti Teknikal Malaysia Melaka

silver nanoparticles required high sintering temperature above 200°C to remove dispersant and solvent, thus limiting their application in flexible substrate such as plastic (Mou *et al.*, 2018). On the other hand, copper is another alternative material which is relatively cheaper than silver. Besides, copper does not tend to have ion migration under an applied voltage.

Non-metal based ink such as carbon nanomaterials such as graphene, fullerene, carbon nanotubes (CNT), and carbon black have been a promising material in nanotechnology. Graphene is a two dimensional (2D) carbon atom with sp2 hybridization and arranged in a hexagonal lattice structure. Graphene has exceptional properties compared to other materials such as carrier mobility of 2.5 × 105 cm2 Vs^{-1}, Young's modulus of 1.0 TPa, and a thermal conductivity above 3000 W/mK (Siqueira and Oliveira, 2016). On the other hand, CNT has a different structure than other carbon allotropes which consist of cylindrical graphene sheet rolled up with a ratio of diameter and length. CNT is classified into two structures which are single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT) as shown in Figure 2.2. Both of the structures have different length and diameter, indicating each has different properties (Thostenson, Ren and Chou, 2001).

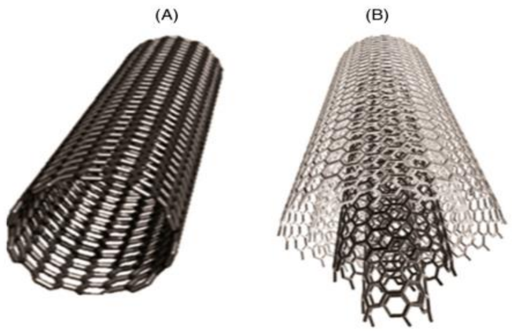

Figure 2.2: (A) Single-walled carbon nanotube (SWNT) structure and (B) a multiwalled carbon nanotube (MWNT). Modified from (Gooding, 2005)

© Universiti Teknikal Malaysia Melaka

2.3 Electrically conductive adhesive

Electrically conductive adhesives (ECAs) are different from other adhesives in term of joining two surfaces with sufficient strength and providing electrical interconnection between the surfaces. ECAs are divided into two categories as shown in Figure 2.3 which are the isotropic conductive adhesives (ICA) and anisotropic conductive adhesives (ACA). ICA conducts electricity in all directions while ACA only conducts electricity in one direction with the device and the conductive substrate (Zhang *et al.*, 2008). These adhesives are used in bonding sensitive materials on circuit boards or antenna structures on RFIDs.

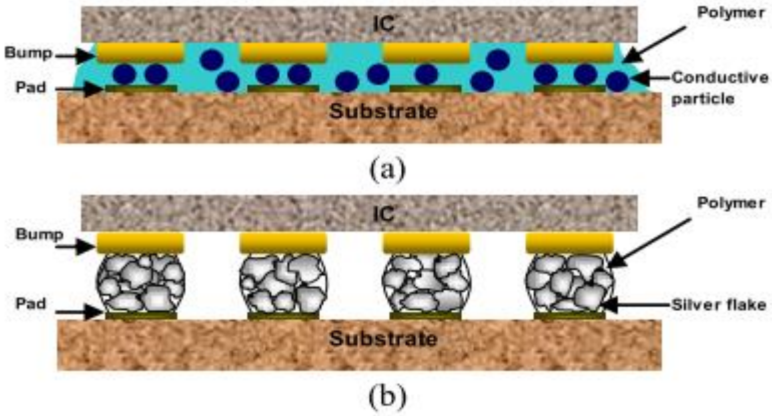

Figure 2.3: Schematic illustrations of (a) ACA and (b) ICA in flip-chip bonding interconnections (Zhang *et al.*, 2008)

Isotropic conductive adhesives (ICA) characteristics essentially depend on types of polymeric binders and conductive fillers. These two components help in providing mechanical strength and the ability to conduct electricity. Materials used as conductive fillers in ICAs to conduct electricity are made of copper, gold, silver and carbon with different sizes and shapes. The most common materials used as a polymeric binder in ICAs are an epoxy resin. The curing condition of a binder is essential to determine the interconnect properties of conductive adhesive to achieve higher reliability (Xiong *et al.*, 2016).

© Universiti Teknikal Malaysia Melaka

Anisotropic conductive adhesives (ACA) are also known as anisotropic conductive film (ACF) and anisotropic conductive paste (ACP). The characteristic of ACA, which only allow electricity travel in vertical axis is due to the well balanced of loading and random distribution of conductive particles in an adhesive matrix (Opdahl, 2016). This unique electric conductivity in ACAs provides some advantages in electronic manufacturing compared with ICAs and other various solder method.

There are two categories of conductive adhesive matrices which are thermoplastic and thermosetting. Thermoplastic consists of long polymer chains with some chains unlinked. Thermoplastic materials able to have polymer flow in high temperature (T_g) since they do not have the cross-link network structure which thermosetting polymer consists (Li and Morris, 1998). During the assembly using thermoplastic material, the control of the temperature must be optimum. In order to obtain good adhesion, the temperature must exceed T_g and precisely low enough to prevent thermal damage to the electric circuit (Lyons and Sujan, 2018). Thermosetting materials is a three-dimensional structure of polymers. Typically, epoxy is used in achieving their adhesive bonding in various types of substrate. Resin and hardener are the main component in epoxy. After the curing process in thermosetting materials, shrinking of particle enable the epoxy achieve stability at longer time and have low contact resistance (Asai *et al.*, 1995).

Commonly, conductive fillers such as carbon black, graphite flake or metallic particles such as silver, copper, nickel and aluminium. The amount of fillers used should be appropriate quantity as large amount will cause the material's mechanical and electrical strength degraded (Li and Morris, 1998). The geometry of the filler can come in various forms, but the most important factors to consider is the adhesion strength of the polymer, the total contact surface between particles and the minimum critical filler concentration to obtain high conductivity (Malliaris and Turner, 1971). Usually, the metallic particles used as filler

© Universiti Teknikal Malaysia Melaka