UNIVERSITI TEKNIKAL MALAYSIA MELAKA

INFLUENCE OF SUSPENSION PREPARATION CONDITION AND MEDIUM MICROSTRUCTURE AND PHASE OF ELECTROPHORETIC DEPOSITED POLY(VINYLIDENE FLUORIDE) FILMS

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

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ABSTRAK

Tesis ini mengenai pencirian PVDF (Polyvinylidene Fluorida) filem aplikasi piezoelektrik untuk menyelesaikan masalah retak kerana ikatan yang lemah antara zarah PVDF yang didepositkan. Objektif eksperimen ini untuk mencirikan penggantungan dan filem PVDF yang disediakan oleh pelarut polimer berbeza (MEK (Methyl Ethyl Ketone) dan DMF (Dimethyl Formamide)), suhu kacau dan masa. Kaedah yang digunakan untuk deposit zarah PVDF pada ITO kaca ialah pemendapan elektroforetik. Ujian pemendapan menunjukkan PVDF yang disediakan dalam penggantungan DMF mempunyai kestabilan tinggi berbanding sampel MEK. Kekasaran permukaan rendah telah ditunjukkan oleh UV-vis Spectra dan SEM dalam filem PVDF yang disediakan menggunakan penggantungan DMF. Filem PVDF yang disediakan menggunakan penggantungan MEK mempunyai filem permukaan yang sangat kasar dan tidak rata berbanding DMF sampel. Filem PVDF yang disediakan menggunakan penggantungan DMF (120˚C, 8 jam) mempunyai permukaan rata dan lebih rendah, walaupun tidak menyeliputi keseluruh kawasan filem. Analisis EDS pada sampel 120˚C, 2 jam dan 120˚C, 8 jam keadaan kacau yang disediakan menggunakan penggantungan DMF menunjukkan kawasan liputan filem PVDF ialah 60.4% bagi 120˚C, 8 jam sampel. Keputusan FTIR menunjukkan filem PVDF yang disediakan menggunakan penggantungan DMF mengandungi β-fasa sahaja, manakala di MEK mengandungi α dan β-fasa. Oleh itu, parameter terbaik filem adalah pada 120˚C, 8 jam yang disediakan menggunakan penggantungan DMF kerana ia mempunyai permukaan filem paling rata berbanding dengan sampel yang lain.

ABSTRACT

This thesis is about the characterization of PVDF (Polyvinylidene Fluoride) film of piezoelectric applications in order to solve the crack problem due to weak bonding between deposited PVDF particles. The objective of this experiment is to characterize PVDF suspensions and PVDF films prepared by different polymer solvents (MEK (Methyl Ethyl Ketone) and DMF (Dimethyl Formamide)), stirring temperatures and time. The method used to deposit the PVDF particles on the ITO glass is electrophoretic deposition. Sedimentation test shows PVDF prepared in DMF based suspension have higher stability when compared with MEK sample. Low surface roughness was shown by UV-vis Spectra and SEM in PVDF films prepared using DMF based suspension. PVDF films prepared using MEK based suspension have a very rough and uneven surface films as compared to DMF derived sample. PVDF film prepared in DMF based suspension (at 120˚C, 8 hr stirring condition) has even and low surface roughness, although did not have fully coverage film area. EDS analysis is used in 120˚C, 2 hr and 120˚C, 8 hr stirring condition that prepared in DMF based suspension show PVDF film coverage area is 60.4% for for 120˚C, 8 hr sample. FTIR results show PVDF films prepared in DMF based suspension contain β-phase alone, while in MEK contain α and β-phase. Therefore, the best parameter of PVDF film is at 120˚C, 8 hr stirring condition prepared in DMF based suspension because it has the most even films' surface compared to other samples.

DEDICATION

I dedicate this report to my frist and second supervisor, Dr. Muhammad Zaimi bin Zainal Abidin and Dr. Lau Kok Tee, thank you for being a guider during this final year project. Thank you for your cooperation and help in the success of this report. Thanks also to my parents for being a pillar of strength for me when I was weak and also to my friends, thank you for not throwing me away when I disappoint you. Thank you for loving me.

Finally, I dedicate this report to my examiners, Associate Prof. Dr. Zulkifli bin Mohd Rosli and Dr. Zurina binti Shamsudin for being my correctors, and also like to dedicate this report to all my respectable lecturers.

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LIST ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

Ba - Barium

$BaTiO_3$ - Barium Titanate

CVD - Chemical Vapour Deposition

DC - Direct Current

DMF - Dimethyl Formamide

$T_{Bp,}$ DMF - Boiling point of DMF

$T_{Ex,}$ DMF - Temperature of DMF that used in the experiment

EDS - Energy Dispersive X-ray Spectroscopy

EPD - Electrophoresis Deposition

FESEM - Field Emission Scanning Electron Microscopy

FTIR - Fourier Transform Infrared

hr - Hour

ITO - Indium Tin Oxide

MEK - Methyl Ethyl Ketone

$T_{Bp,}$ MEK - Boiling point of MEK

$T_{Ex,}$ MEK - Temperature of MEK that used in the experiment

O - Oxygen

OM - Optical Microscope

Pb - Lead

PVD	-	Physical Vapour Deposition
PVDF TeFE	-	PVDF Tetrafluoroethylene
PVDF TrFE	-	PVDF Trifluoroethylene
PVDF	-	Polyvinylidene Fluoride
PZT	-	Lead Zirconate Titanate
SEM	-	Scanning Electron Microscopy
Ti	-	Titanium
U.S	-	United State
UV	-	Ultraviolet
Zr	-	Zirconia

CHAPTER 1

INTRODUCTION

1.0 Introduction

This chapter will introduce the history of piezoelectric, problems statement, objectives, and scopes of project. All the materials involved in piezoelectric properties, especially piezoceramics and piezopolymers also cited in this chapter.

1.1 History and Background

When a piezoelectric substance is deformed, electric potential is generated. It is called piezoelectric effect. It was demonstrated by the brothers Pierre Curie and Jacques Curie in 1880 (Manbachi et al., 2011). Certain materials can generate a voltage when placed under stress, such as quartz, salt and sugar. These materials had crystal structures with asymmetric dipole moments that would respond to mechanical pressure (Morgan Advance Materials, 2009).

The crystalline structure produce a voltage proportional to the applied mechanical pressure when the crystals are exhibiting direct piezoelectric effect, which is electricity generated from applied stress. Vise-versa, the material exhibits the converse piezoelectric effect, a stress is generated in response to applied electric field (Jacques and Currie, 1881).

In 1945, ferroelectric ceramics were used as capacitor materials, because of its high dielectric strength. First ceramic to be discovered is quartz, followed by $BaTiO_3$ (Barium Titanate) and then PZT (Lead Zirconate Titanate). The ceramics are also exhibiting high piezoelectric constant. However, they have several disadvantages, which are high melting point and low flexibility. Besides, PZT contains toxic lead element.

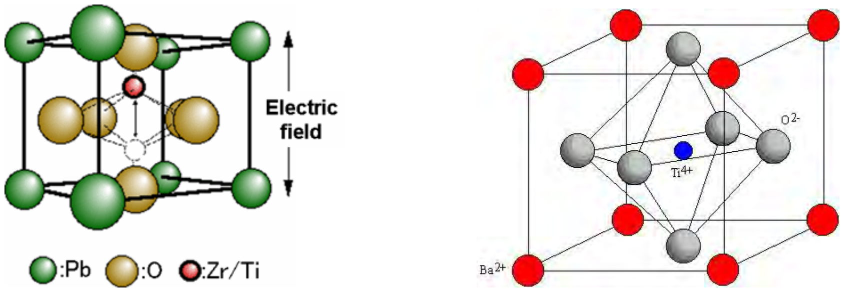

Figure 1.1: PZT (Lunes, 2010) and $BaTiO_3$ structures (Oren, 1999).

Figure 1.1 shows the crystal structures of $BaTiO_3$ and Pb (Zr, Ti)O_3. PZT consists of one part of Pb (Lead), one part of Zr (Zirconia) and Ti (Titanium) and three parts of and O (Oxygen). Although PZT has higher permittivity and better crystal structures as piezoelectric applications than $BaTiO_3$, the PZT is toxic. For $BaTiO_3$, it consists of one part of the Ba (Barium), one part of Ti and three parts of O. They still cannot fulfill the mechanical flexibility requirement of piezoelectric applications.

Then, new piezoceramic families and several types of piezoceramic signal filters were developed such as television, radio and communications equipments were created (Piezo Systems, Inc. 1994). The commercial success of the Japanese efforts has attracted the attention of the industry in many other nations and spurred a new effort to develop successful piezoceramic products in 1980.

In 1969, Kawai has found a strong piezoelectricity in PVDF (Polyvinylidene Fluoride) and it used as an alternative candidate to PZT and $BaTiO_3$ (Kawai and Heiji, 1969). Piezoceramic materials like PZT and BaTiO3 suffer from mechanical strength and flexibility issues since they are brittle. Besides that, PZT also contain lead that can harm human body. Because of that, these materials were replaced with PVDF. PVDF has no lead content, requires low processing temperature and has good mechanical flexibility. Although PVDF has a better mechanical properties compared to PZT and BaTiO3 vibration sensor application, difficulties might occur in the produce PVDF thick film. Then, other PVDF co-polymers were also reported by Tasaka and Miyata in 1985, including PVDF TrFE (Trifluoroethylene) and PVDF TeFE (Tetrafluoroethylene) (Cohen et al., 1996). The search for perfect piezo material is still going on until now, because the materials that used today still cannot beat the PZT material. Researchers are trying to find the materials that did not contain lead, such as polymer materials.

The piezoelectric material was fabricated in the form of thick film for the purpose of poling process at much higher applied voltage. PVDF is an inert material and need to be poled for piezoelectric applications (Lin et al., 2002). The poling of piezoelectric material is to create electric polarization inside the material so that sufficient ferroelectric strength is achieved for application (Kok et al., 2014). Table 1.1 shows the history of piezomaterials discovery and development over the years. Although many materials that found in nature, have piezoelectric properties, there are gaps between the material properties and the application requirement. Because of these circumstances, development of better piezoelectric is still been continued to improve the properties to fill the needs of the applications.

Table 1.1: Discovery of piezoelectric materials and their mechanisms or applications (Katzir, 2012).

Years	**Materials**	**Mechanisms/Applications**
1880	Tourmaline, Topaz, Quartz, Rochelle Salt and Cane Sugar	Discovery of electrical charge voltage generated is proportional to the applied mechanical stress on the crystals.
1881	-	Piezoelectric effect was mathematically deduced from fundamental thermodynamic principles.
1917	Quartz	The converse piezoelectric effect was used in the first submarine detecting-sonar.
1920 - 1940	Natural Crystal	The first generation applications were produced. Resonating and non-resonating piezoelectric devices.
1939 - 1945	$BaTiO_3$ and PZT	These materials possessed superior dielectric and piezoelectric properties as compared to quartz.
1951	$BaTiO_3$ and PZT	Piezoceramic signal filters, which addressed needs arising in television and radio.
1952	$BaTiO_3$ and PZT	$BaTiO_3$ have been replaced by PZT.
1969	PVDF	This material was found as a piezoelectric material because it has a strong piezoelectricity. Consider as a replacement for PZT and $BaTiO_3$.

1.2 Problem Statement

PVDF film deposition faced the crack problem due to weak bonding between PVDF particles, in additional to high residue stresses (Razi, 2014). The densification process by heat treatment did not resolve the cracks problem because of poor bonding between deposited particles. To solve the problems, the improvement of the density of PVDF layer without heat treatment is needed to avoid the crack. The most important issue is the bonding between the deposited polymers must be strong enough to hold the coating. In addition, the substrate for the deposited film must undergo a surface heat treatment using an acid in order to achieve good adhesion between film and substrate.

EPD (Electrophoresis Deposition) has a capability to deposit a multilayer film on complex surface morphologies in a conformal manner at a high deposition throughput, but only with low cost and simple equipment set-up (Foster and White, 2002). However, the properties of the polymeric PVDF film deposited by EPD for accelerometer sensor such as thickness, density, and adhesion, are depended on chemicals formulation and process parameters of the EPD. As the process of EPD involved many parameters such as materials, substance design, formulation, EPD process, annealing temperature and time, study is required to characterize properties of the deposited film, so that an optimization of these parameters to obtain PVDF film with adequate mechanical properties to perform well as the cantilever of an accelerometer sensor (Razi, 2014).

1.3 Objectives

In order to synthesize crack-free PVDF thick film, the current study embarks on the following objectives:

1. To characterize PVDF suspension prepared by different suspension formulations, processing temperatures and times.

2. To characterize the surface morphology, cross-sectional microstructure and phase composition of PVDF film electrophoretic deposited using the PVDF suspensions stated in objective 1.

1.4 Scopes

In this research, PVDF film will be deposited by EPD method using different PVDF suspension formulation, as well as suspension processing temperatures and times.

To produce a PVDF film, three phases must be completed. The first phase is the preparation of PVDF suspension in organic solvent. For second phase, PVDF suspension was deposited by EPD method on the ITO (Indium Tin Oxide) glass substrate. The last phase is characterizations of the filmed sample. Different parameters will produce PVDF films with different surface morphology, cross-sectional microstructure and phase composition. The appearance of the PVDF particles on the substrate also can be analyzed. Fixed EPD parameters are used for the deposition of all PVDF films. The film will be characterized by using OM (Optical Microscope), FTIR (Fourier Transform Infrared), UV-Visible spectroscopy (Ultraviolet-Visible Spectroscopy) and SEM (Scanning Electron Microscopy).

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter is about the properties of the PVDF, which used as piezoelectric components. Beside that, the methods and mechanisms involved also cited in this chapter.

2.1 General Material Properties of PVDF

PVDF crystal structures consist of Fluorine, Carbon and Hydrogen elements (refer Figure 2.1). It used as a piezoelectric material to replace $BaTiO_3$ and PZT that contain lead. By reason of a broad, general properties of the material should be reviewed in advance to ensure it can meet the application requirements. Table 2.1 shows several general properties of PVDF. PVDF contain several unique properties that are not owned by $BaTiO_3$ and PZT. Because of that, PVDF has received particular attention. One of the most important features is that the PVDF can be easily produced in the form of large thin, flexible sheets and in variety of shapes. The low dielectric permittivity and elastic stiffness of PVDF films at room temperature, resulting in high voltage sensitivity and low acoustic impedance make them attractive for application in piezoelectric devices (Choudhary and Patri, 2009).

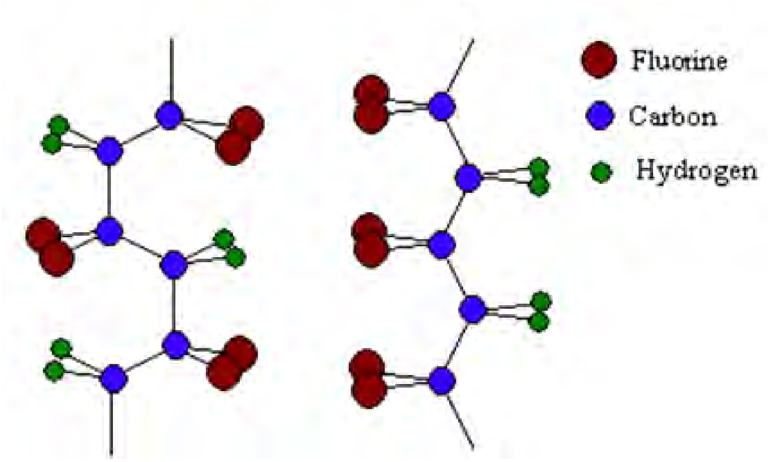

Figure 2.1: Crystal structures of PVDF (Plastics Europe, n.d.).

Table 2.1: General properties of PVDF (Frank, 2014).

Properties	**Descriptions**
Chemical resistance	PVDF is made of composite fluoropolymer resin and ceramic pigment, making it a good chemical resistance coating.
Low melting point 177°C	PVDF is an easy melted material and have a low melting point. It's also easy to be processed compared to other fluoropolymers.
Low density ($1.78\ g/cm^3$)	PVDF can be molded and is commonly used in the chemical and semiconductor as well as lithium ion batteries. It is also available as a crosslink closed cell foam which used increasingly in aviation and aerospace applications.
UV resistance, thermal degradation (exposure to 149°C).	It have very high fade resistance and ultraviolet resistance in extremely harsh environment. This will allow PVDF to withstand the surrounding temperature as a film in piezoelectric sensor.
High mechanical strength and flexibility	PVDF structures have the most stable chemical bond because of the fluoride-carbon bond.

Table 2.2 shows the comparison of smart materials and it is shown piezoelectric polymers are much more durable and sensitive in responding to deformations than ceramics, and also better electric fields. These polymers are not the common that used in polymer films, but used as extreme piezoelectric at the moment. However, PVDF has piezoelectric voltage coefficient 20 times greater than the more common ceramic crystal (Esterly, 2002).