UNIVERSITI TEKNIKAL MALAYSIA MELAKA (UTeM)

ELECTROPHORETIC DEPOSITION AND ANNEALING OF POLY(VINYLIDENE FLUORIDE)-GRAPHITE LAMINATED COMPOSITE FILM

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

by

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DECLARATION

I hereby, declared this report entitled ‘electrodeposition and annealing of poly(vinylidene fluoride)-graphite laminated composite film’ is the results of my own research except as cited in references.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment to the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

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ABSTRACT

In this report, the electrophoretic deposition (EPD) of PVDF-graphite composite is investigated. Process of EPD involved many parameters such as materials, substrate 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. The objectives in this project are to sequentially deposit graphite composite-PVDF-graphite composite laminated composite film on stainless-steel substrate using EPD method and to strengthen structure of the composite film through ambient annealing process. There are 3 phases in this project which are optimization of suspension formulation and EPD parameters, the synthesis PVDF/graphite-layered composite film and the last phase is the characterization and evaluation of the piezoelectric properties of PVDF/graphite composite film. After the characterization, the best parameter and formulation of suspension has been decided which are 95 mL EMK + 5 mL distilled water + 1g of PVDF powder for PVDF suspension and 80 mL acetone + 20 mL butylamine + 0.1 g of graphite powder + 0.3 g of PVDF powder for graphite composite suspension. The parameter for annealing process also has been chosen for healing the cracks occurred on the composite film after the deposition which is anneal at 150˚C for 60 minutes.

ABSTRAK

Dalam laporan ini, pengenapan (EPD) daripada PVDF-grafit komposit disiasat. Proses EPD melibatkan banyak parameter seperti bahan-bahan, reka bentuk substrat, formulasi, proses EPD, suhu penyepuhlindapan dan masa, kajian diperlukan untuk mencirikan sifat-sifat filem yang terhasil, pengoptimuman parameter ini untuk mendapatkan filem PVDF dengan sifat-sifat mekanikal yang mencukupi. Objektif projek ini adalah untuk berurutan deposit grafit komposit-PVDF-grafit komposit berlapis filem komposit pada substrat keluli tahan karat menggunakan kaedah EPD dan untuk mengukuhkan struktur filem komposit melalui proses penyepuhlindapan ambien. Terdapat 3 fasa dalam projek ini yang mengoptimumkan formulasi penggantungan dan parameter EPD, sintesis PVDF/grafit filem komposit dan fasa terakhir adalah pencirian dan penilaian sifat-sifat piezoelektrik daripada PVDF/grafit filem komposit. Selepas pencirian, parameter yang terbaik dan formulasi optimum adalah 95 mL EMK + 5 mL air suling + 1 g serbuk PVDF bagi campuran PVDF dan 80 mL aseton + 20 mL butylamine + 0.1 g serbuk grafit + 0.3 g serbuk PVDF bagi campuran grafit komposit. Parameter untuk proses penyepuhlindapan juga telah dipilih untuk penyembuhan retak berlaku pada filem komposit selepas pemendapan yang sepuh lindap pada 150˚C selama 60 minit.

DEDICATION

To my parents and family members for their continuous support throughout my study.

To my supervisor and co-supervisor for his advice and guidance in completing this research.

To all my friends for their continuous support and help in completing this report.

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%	-	Percent
µm	-	Micrometer
Al_2O_3	-	Aluminum Oxide
$BaTiO_3$	-	Barium Titanate
CaO	-	Calcium Oxide
DC	-	Direct Current
DMF	-	Dimethylformamide
DSC	-	Differential Scanning Calorimetry
EMK	-	Ethyl Methyl Ketone
EPD	-	Electrophoretic Deposition
FKP	-	Fakulti Kejuruteraan Pembuatan
g	-	Gram
g/cm^3	-	Gram / Centimeter Cubic
ICP	-	Integrated Circuit Piezoelectric Sensor
IEPE	-	Integral Electronic Piezoelectric
$MoSi_2$	-	Molybdenum Disilicide
Ni	-	Nickel
^oC	-	Degree Celcius

^oF	-	Degree Fahrenheit
OM	-	Optical Microscope
PC	-	Personal Computer
PVDF	-	Poly(vinyliden fluoride)
PZT	-	Lead Zirconate Titanate
RMS	-	Root Mean Square
SEM	-	Scanning Electron Micoscope
SEM	-	Scanning Electron Microscopy
UTeM	-	Universiti Teknikal Malaysia Melaka
V	-	Volt
Wt%	-	Weight percent
XRD	-	X-Ray Diffraction
ZrO_2	-	Zirconium Dioxide

CHAPTER 1
INTRODUCTION

1.1 Background

Piezoelectric in the accelerometer sensor has been studied widely and many material of composite has been used in order to maximize the sensitivity of the piezoelectric. Most commonly used material is Polymeric poly(vinyliden fluoride) (PVDF) because of it has potential for the candidate of a flexible vibration sensor with higher piezoelectric stress constant and low elastic stiffness. So PVDF has advantages in the producing higher sensitivity sensors as compared to the ceramic piezoelectric counterpart according to Kok (2011). PVDF piezoelectric sensor has a better mechanical flexibility and requires lower fabrication temperature as compared to the widely used lead zirconate titanate (PZT) and barium titanate ($BaTiO_3$). Although PVDF-based sensor has been commercially available on nowadays application, its piezoelectric performance lowers than the ceramic counterpart. Studies have showed that superior piezoelectric properties can be obtain or achieved by free standing piezoelectric film compared to the piezoelectric film integrated onto the supporting substrate.

EPD is essentially a two-step process. In the first step, particles suspended in a liquid are forced to move toward an electrode by applying an electric field to the suspension (electrophoresis). In the second step, the particles collect at one of the electrode and form a coherent deposit on it. It should be noted that the process yields only a powder compact, and therefore electrophoretic deposition should be followed by a densification step such as sintering or curing in order to obtain a fully dense material.

This study will provide lower cost fabrication and high performance cantilever-based accelerometer for the motion or vibration sensor application. Besides that, graphite will be used as the electrode as a replacement to silver-palladium which is very expensive and graphite will provide optimum thickness for the polarization stage and piezoelectric performance. This study also will determine the relationship of EPD parameters and suspension formulation on the deposit yield, thickness and the microstructure of the PVDF and graphite composite film.

1.2 Problem Statement

EPD has a capability to deposit multilayer film on complex surface morphologies in a conformal manner at a high deposition throughput, but only with a low cost and simple equipment set-up based on Foster (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, substrate 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.

As for the electrode, the silver-palladium electrode will be replaced by graphite electrode to enhance its resistivity, thermal conductivity, and thermal shock as well as its sensitivity. This also will reducing the cost as the silver-palladium (Ag-Pd) will cost more for anyone whose progressing the project. Graphite platelets will be used for synthesizing of graphite electrode so the challenging part is to maintaining the electrical properties throughout the vibration process. The using of graphite blended with conducting polymer will be possible.

Another challenge is to synthesize a simple PVDF cantilever sandwiched between graphite electrodes, or a PVDF-graphite multilayer cantilever. This can be done changing the EPD suspension or solution from graphite to PVDF and then to graphite again sequentially to deposit the layer according to the design of the composite. The structure or the layer of the composite will be reinforced by a subsequent annealing process.

1.3 Objectives

In order to synthesize steel-supported piezoelectric PVDF thick film sandwiched by graphite electrodes, the following objectives are set:

(a) To sequentially deposit graphite composite-PVDF-graphite composite laminated composite film on stainless-steel substrate using EPD method.

(b) To strengthen structure of the composite film through ambient annealing process.

1.4 Scope

This project consist of three phase which are preparation of suspension, deposition and lastly characterization. In the first phase, suspension of graphite and suspension of PVDF will be prepared according to the parameter. While in the second phase which is deposition, each deposited layer will be undergo annealing process to make the structure of the layer become firm on the steel substrate. The deposition PVDF/electrode -layered composite film will be deposited by EPD, where first electrode layer, PVDF layer, and second electrode layer will be deposited sequentially by changing the EPD from graphite to PVDF layer and then back again to graphite.

Final layer of the composite will be annealed through different temperature from 125˚C to 180˚C to see what will be the effect of the annealing temperature to the microstructure of the surface. The separation between the two electrodes is 1cm which is constant from beginning of the project until the end. Then the last phase is characterization where the sample will be analyze by using optical microscope and scanning electron microscope. Temperature of the suspension while being deposited is at room temperature.

CHAPTER 2

LITERATURE REVIEW

2.1 Piezoelectric Accelerometer Sensor

Vibration and shock are present in all areas of our daily lives and routines. They may be transmitted and generated by turbines, motors, machine-tools, towers, bridges, and even by the body of human. While some vibrations are desirable, others may be destructive or even disturbing. Consequently, there is often a need to study and understand the causes of vibrations and to develop methods to measure and control them. The accelerometer sensor serves as a link between vibrating structures and electronic measurement equipment. It converts the mechanical forces into electronic data so the amount of the force can be measured.

There are many different types of accelerometers and each has unique characteristics, advantages and disadvantages. It have different technologies and also different design based on what application it is used. Among the technologies it used are piezoelectric accelerometer, piezoresistive accelerometer and strain gage based accelerometer. The piezoelectric accelerometer is used to measure the dynamic changes such as acceleration, vibration, and mechanical shock. Piezoresistive accelerometer change in the electrical resistivity of a semiconductor or metal when mechanical strain is applied. While a strain gauged accelerometer is based on detecting the deflection of a seismic mass by using a silicon or foil strain gauge element.

Piezoelectric accelerometers are used in many applications, environments and different industries. Piezoelectric measuring devices and systems are widely used today on the production floor, in laboratory and as original equipment for recording and measuring dynamic changes in mechanical variables including vibration and shock. It is installed in cars to study shock and vibrations, used in camcorders for the image stabilization, and also used in cameras for anti-blur capturing and used in mobile phones for multiple functions including tilt detection and motion detection. Some accelerometers have built-in electronics to amplify the signal before transmitting it to the recording device. These devices usually obey with the IEPE (Integral Electronic Piezoelectric) standard or its proprietary equivalent, ICP (Integrated Circuit Piezoelectric Sensor). The applications of piezoelectric materials can be categorized into sensors, actuators, transducers and generators depending on the type of piezoelectric effect. Sensors make use of the direct piezoelectric effect, transforming mechanical energy into measurable voltage signal. If the output power from this conversion is large enough to power microelectronic devices, it can therefore be used as a micro generator. Actuators transform electrical into mechanical energy by means of the inverse piezoelectric effect. Finally, transducers use both effects to operate as single devices.

2.1.1 Type of Piezoelectric Accelerometer Sensor

Piezoelectric accelerometer sensor can be categorized into three types: (i) shear, (ii) compression, and (iii) bender. A shear-type accelerometer as shown in Figure 2.1 is an accelerometer where the seismic mass is attached to the piezoelectric crystal so that it exerts a shear load on the crystal rather than a compressive load. It feature sensing crystals attached between a center post and a seismic mass. A compression ring or stud applies a pre-load force to the element assembly to insure a rigid structure and linear behavior. Under acceleration, the mass causes a shear stress to be applied to the sensing crystals. This stress results in a proportional electrical output by the piezoelectric material.

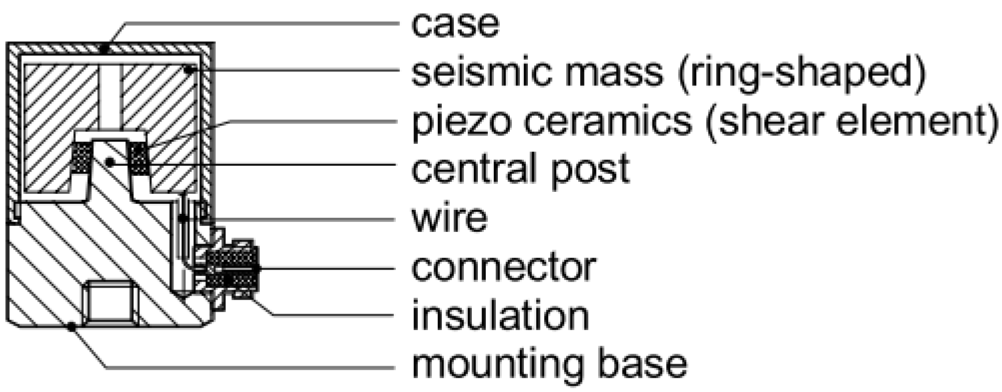

Figure 2.1: Shear Type Accelerometer (Metra Mess- und Frequenztechnik, 2001)

The compression-type accelerometers (as refer in Figure 2.2) offer simple structure, historical availability and high rigidity. The compression designs sandwich the piezoelectric crystal between a seismic mass and rigid mounting base. A screw or an elastic stud secures the element of sensing to the mounting base. When accelerating the sensor, the seismic mass decrease or increase the amount of force acting upon the crystal, and will resulting a proportional electrical output. Due to their inherently the stiff structure, the accelerometer will offers high resonant frequencies, that will causing in a broad, accurate frequency response range. This design is generally can withstand high g-shock (gravity-shock) levels and very rugged. However, due to the intimate contact of the external mounting base with the sensing crystals, the accelerometer tend to be more sensitive to base bending because of strain and thermal transient effects. These effects can contribute to wrong output signals when used on a low frequencies in thermally unstable environments, such as near fans or outdoors and blowers or at a thin, sheet-metal structures.

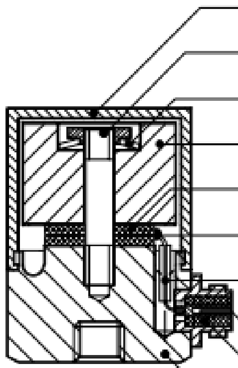

Figure 2.2: Compression Type Accelerometer (Metra Mess- und Frequenztechnik, 2001)

Piezoelectric bending actuators (or piezoelectric cantilevers, or piezoelectric bimorphs) as shown in Figure 2.3 bear a close resemblance to bimetallic benders. The application of an electric field across the two layers of the bender result in one layer to contracts, while the other to expand. The result is a curvature much greater than the thickness or length deformation of the individual layers. With a piezoelectric bender, relatively high displacements can be achieved, but at the cost of force and speed. There are some benders that have only one piezoelectric layer on top of a metal layer (unimorph), but generally there are two piezoelectric layers and no metal (bimorph). This way, the displacement is doubled in comparison to a single layer version. If the number of piezoelectric layers exceeds two, the bender is referred as a multilayer. With thinner piezo layers, a smaller voltage is required to produce the same electric field strength, and therefore, the benefit of the multilayer benders is their lower operating voltage.

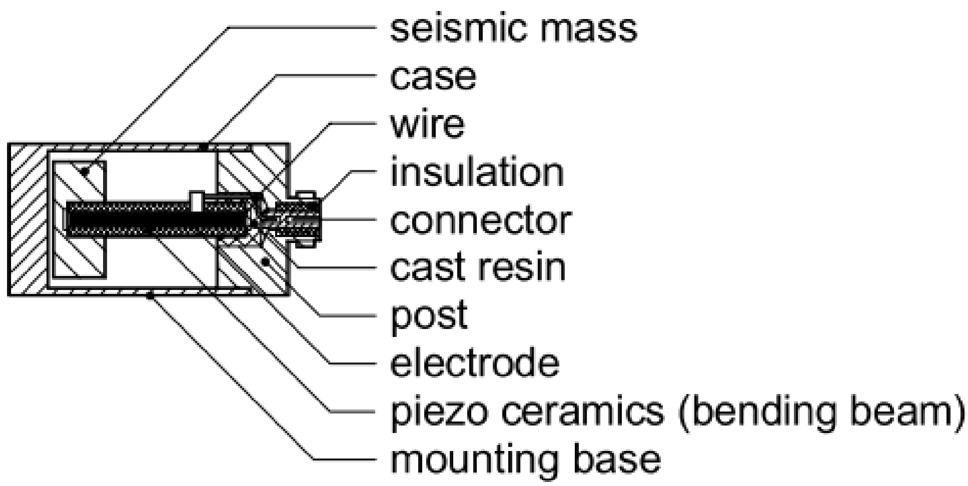

Figure 2.3: Bender Type Accelerometer (Metra Mess- und Frequenztechnik, 2001)

2.1.2 Comparison of Different Types of Accelerometer

The reason for using different piezoelectric systems is their individual suitability for various measurement tasks and varying sensitivity to environmental influences. The following table shows advantages and drawbacks of the accelerometer type discussed in section 2.1.1:

Table 2.1: Advantages and Disadvantages of Accelerometer Designs (Metra Mess- und Frequenztechnik, 2001)

	Shear	Compression	Bender
Advantages	• Low temperature transient sensitivity • Low base strain sensitivity	• High sensitivity to mass ratio • Robustness • Technologi-cal advantages	• Best sensitivity to mass ratio