CHARACTERIZATION OF FILLED EPOXY THIN FILM COMPOSITES FOR DIELECTRIC APPLICATION

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CHARACTERIZATION OF FILLED EPOXY THIN FILM COMPOSITES FOR DIELECTRIC APPLICATION

by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles “Characterization of Filled Epoxy Thin Film Composites for Dielectric Application”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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Date:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

PCB	Printed Circuit Board
CMC	Critical Micelle Concentration
$CaCO_3$	Calcium Carbonate
$BaTiO_3$	Barium Titanate
CNT	Carbon Nanotube
SWCNT	Single-walled Carbon Nanotube
MWCNT	Multi-walled Carbon Nanotube
BSTZ	Barium Strontium Titanate Zirconium
Ag	Silver
Al	Aluminium
DGEBA	Bisphenol-A Diglycidylether
PMMA	Polymethyl Methacrylate
PTFE	Polytetrafluoroethylene
Triton X-100	Polyoxyethylene Octyl Phenyl Ether
SDS	Sodium Dodecyl Sulfate
CTAB	Cetyltrimethylammonium Bromide
AMPTES	3-(Aminopropyl)triethoxysilane
GPTMS	3-Glycidoxypropyltrimethoxy Silane
H_2O_2	Hydrogen Peroxide
CO_2	Carbon Dioxide
DI	Deionized Water
TEM	Transmission Electron Microscope
HRTEM	High Resolution Transmission Electron Microscope
SEM	Scanning Electron Microscope

DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DTG	Derivative Thermogravimetric
TMA	Thermomechanical Analysis
CTE	Coefficient of Thermal Expansion

LIST OF SYMBOLS

Q	Charge
V	Voltage
C	Capacitance
ε	Permittivity of the Material
ε_0	Permittivity of the Vacuum
k	Dielectric Constant
A	Area
d	Separation between Two Conductors
t	Thickness of the Specimens
V_f	Volume Fraction of Filler
V_m	Matrix Volume Fraction
W_f	Weight of Filler
W_m	Weight of Matrix
$W_{surfactant}$	weight of surfactant
W_{AMPTES}	weight of AMPTES
ρ_f	Density of Filler
ρ_m	Density of Matrix
E_f	Filler Modulus
E_m	Matrix Modulus
E’	Storage Modulus
E’’	Loss Modulus
I_D	Intensity Ratio of D Band
I_G	Intensity Ratio of G Band
T_g	Glass Transition Temperature

T_5	5 % Weight Loss Temperature
T_{onset}	Onset Degradation Temperature

LIST OF APPENDICES

PENCIRIAN KOMPOSIT FILEM NIPIS EPOKSI TERISI UNTUK KEGUNAAN DIELEKTRIK

ABSTRAK

Dalam kajian ini, sifat dielektrik, mekanikal dan terma komposit filem nipis epoksi terisi pelbagai jenis pengisi telah dikaji. Bahan pengisi dan epoksi disediakan dengan menggunakan pencampuran ultrasonik dan komposit filem nipis difabrikasi dengan kaedah lapisan putaran. Dalam peringkat petama, komposit filem nipis epoksi terisi mineral kalsium karbonat (mineral $CaCO_3$) dan kalsium karbonat termendak ($CaCO_3$ termendak) telah dikaji. Adalah didapati bahawa $CaCO_3$ termendak mempamerkan sifat dielektrik dan kekuatan tensil yang lebih baik manakala mineral $CaCO_3$ mempamerkan sifat terma dan moduli yang lebih baik. Dalam peringkat kedua, sifat bagi pelbagai jenis pengisi ($CaCO_3$ termendak, barium titanat ($BaTiO_3$) and tiubnano karbon berbilang dinding (MWCNT)) telah dikaji. Adalah didapati bahawa $BaTiO_3$ dan MWCNT mempamerkan sifat dielektrik dan kemuatan yang lebih baik dibandingkan dengan $CaCO_3$ termendak. Memandangkan sifat dielektrik dan kemuatan adalah penting untuk kegunaan kapasitor, MWCNT dipilih untuk kajian kefungsian dalam peringkat ketiga. Rawatan MWCNT oleh pelbagai jenis kefungsian mengunakan polioksietilena oktil fenil eter (Triton X-100), natrium dodesil sulfat (SDS), and 3-(aminopropil)trietoksil silana (AMPTES)) digunakan untuk merawat MWCNT. Adalah didapati bahawa rawatan MWCNT mempunyai sifat dielektrik dan mekanikal lebih baik daripada MWCNT tanpa rawatan. Sifat dielektrik yang lebih kurang sama diperhatikan dalam perbandingan bagi dua jenis epoksi (OP 392 epoksi dan DER 332 epoksi) dengan 1.5 vol% MWCNT tanpa rawatan dan MWCNT dengan rawatan oleh Triton X-100 dan SDS. Komposit filem nipis OP 392 epoksi mempamerkan suhu peralihan kaca (T_g) yang tinggi dan kekuatan tensil yang lebih rendah dibandingkan dengan komposit filem nipis DER 332 epoksi. Secara keseluruhannya, komposit filem nipis epoksi terisi MWCNT dengan rawatan oleh Triton X-100 adalah bahan yan paling sesuai untuk kegunaan dielektrik.

CHARACTERIZATION OF FILLED EPOXY THIN FILM COMPOSITES FOR DIELECTRIC APPLICATION

ABSTRACT

In this research, dielectric, mechanical and thermal properties of various types of fillers filled epoxy thin film composites were studied. The fillers and epoxy were prepared using ultrasonic mixing and the thin film composites were fabricated using spin coating method. In the first stage, the properties of mineral calcium carbonate (mineral $CaCO_3$) and precipitated calcium carbonate (precipitated $CaCO_3$) filled epoxy thin film composites were investigated. It was found that precipitated $CaCO_3$ exhibited higher dielectric properties and tensile strength than mineral $CaCO_3$ whereas mineral $CaCO_3$ exhibited higher thermal properties and modulus than precipitated $CaCO_3$. In the second stage, the properties of various types of fillers (precipitated $CaCO_3$, Barium titanate ($BaTiO_3$) and multi-walled carbon nanotube (MWCNT)) were investigated. It was found that $BaTiO_3$ and MWCNT exhibited higher specific capacitance and dielectric constant than precipitated $CaCO_3$. Since dielectric and capacitance properties are important for the capacitor application, MWCNT was chosen in the functionalization study in the third stage. Various types of functionalization using polyoxyethylene octyl phenyl ether (Triton X-100), sodium dodecyl sulfate (SDS), and 3-(aminopropyl)triethoxy silane (AMPTES) treated MWCNT were used to treat MWCNT. It was found that treated MWCNT had improvement in dielectric and mechanical properties. Slightly similar dielectric properties were observed in the comparison of two different epoxies (DER 332 epoxy and OP 392 epoxy) with 1.5 vol% untreated MWCNT and Triton X-100 and SDS treated MWCNT. OP 392 epoxy thin film composites exhibited higher glass transition temperature (T_g) and lower tensile strength compared to that of DER 332 epoxy thin film composites. Overall, Triton X-100 treated MWCNT filled OP 392 epoxy thin composite is the most suitable material for the dielectric application.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Electronic technology industry becomes a critical demand for human being in 21st century (Luo, 2012). In fact, electronics are one of the technologies that are widely used in all over the world as it brings our lives convenient and easy. All of our gadgets and machines like computers are being produced with electronic application. In recent few years, electronic equipment is having greater functionality in smaller size. It forces the power conversion system to adapt miniaturization, efficiency improvement, reliability and minimum cost. Latest electronics technology products such as smart phone, tablets tend to design in thinner form. This is because the functionalities of high performance digital devices become more diverse and requires more function to be concentrated into a thin and compact housing.

The performance of electronic device has been rapidly growing in order to develop smaller electronic products with high compact and reliability electronic devices. It has been reported nearly 80% of printed circuit board (PCB) is occupied by passive components such as transistor, capacitor, diode, etc, that is incapable in power gain (Wu *et al*., 2009). As a result, current researches are still developing the passive components so that the number of passives components is growing steadily with high functionality of electronic devices. Many researchers have investigated on embedded passive component which is able to replace the discrete passive component. They have found that the advantages of embedded passive component are save cost, improve board reliability and increase free up space (Wu *et al.*, 2009; Lu *et al.*, 2007; Cho *et al.*, 2004; Alam *et al.*, 2007; Kim *et al.*, 2007; Lu & Wong, 2008). Among passive components, capacitor plays important role in electronic device which is used to store energy in electric field.

In previous work, the embedded capacitor was formed in the form of thin film composite and laminate into PCB (Peiffer, 2001). These films can reduce the usage of discrete surface mount capacitors by extend them throughout the PCB board. The embedded capacitor consists of thin dielectric material sandwiched between two conductive elements such as copper, conductive metal and polymer. The dielectric material is insulator which has high dielectric constant and low dielectric loss whereas the conductive layers serve as power and ground plane for embedded capacitor application (Alam *et al.*, 2007). The most important requirement for embedded capacitor material is high dielectric constant, low dielectric loss and low cost that the current research efforts to develop and tends to fulfill the requirement of capacitor.

Polymer thin film composite is a candidate material that can be used as dielectric layer of embedded capacitor. The reason of using polymer as dielectric in electronic device is because polymer meet requirement of low temperature processability (Lu *et al.*, 2007). Polymer also provides strong resistivity, insulation resistance and high temperature resistance (Alias, 2012). Epoxy is thermoset polymer that widely used as dielectric material in electronic industries. This is because epoxy has unique chemical and physical properties. However epoxy itself has low dielectric constant which is not suitable to use in capacitor application. As a result, high dielectric constant filler (high k) is introduced to mix with epoxy matrix to produce high k- dielectric materials (Alam *et al.*, 2007).

1.2 Problem Statements

Fillers with high dielectric properties are required to be used in capacitor application. Barium titanate ($BaTiO_3$) has been used as filler in polymer composites for capacitor application since it exhibits ferroelectricity that provides high polarization and high dielectric constant (high-k) (Wang, 2002). Even though $BaTiO_3$ is favorable dielectric materials for capacitor application, but the cost of $BaTiO_3$ is expensive. In order to solve this problem, filler materials with low cost are getting acceptance to reduce the cost of fabricating dielectric materials. Calcium carbonate ($CaCO_3$) with dielectric constant of 9 is getting acceptance for the application as dielectric materials. Meanwhile multi-walled carbon nanotube (MWCNT) is another candidate to be used as filler for dielectric material. Although MWCNT is an expensive filler material, but MWCNT produces high dielectric constant value compare to the $BaTiO_3$. The dielectric properties of MWCNT polymer composites have been studied by many researches, but limited research has been done on capacitor. As a result, in this study, $BaTiO_3$ is used as reference since it is widely used in the industry, whereas $CaCO_3$ is used to reduce the cost of the dielectric material and MWCNT is used to achieve higher dielectric constant of the dielectric material.

MWCNT is focused in this study due to unique properties of MWCNT that exhibit high dielectric constant and capacitance. However, many researchers have reported that MWCNT tends to form agglomeration due to van der Waals forces exists between MWCNT (Geng *et al.*, 2008a). The inhomogeneous MWCNT in polymer composites generally affects the properties in the composites. In order to improve filler – polymer interaction, filler functionalization is introduced to enhance the adhesion between fillers and polymer matrix. This functionalization can improve the dispersion of filler throughout polymer composite. The surface treatment of MWCNT can be done by introducing surfactant treatment. The surfactant is used to treat the surface of MWCNT by formation of micelles above critical micelle concentration (CMC) and absorb on the surface of MWCNT to overcome the van der Waals attraction of MWCNT (Geng *et al.*, 2008a). Meanwhile silane treatment is also another method to functionalize MWCNT and improve the interaction between MWCNT with epoxy matrix (Santos *et al.*, 2011). Based on literature review, functionalization by surfactant and silane coupling agent have been studied in previous research, however combination functionalization of surfactant with silane coupling agent treated MWCNT are minimal.

Even though high dielectric constant is important for dielectric material, but selection of suitable epoxy resin is also important for electronic packaging application. Thermosetting polymer such as epoxy with high glass transition temperature (T_g) is required to be used in electronic packaging application. This is because high glass transition temperature (T_g) of epoxy has ability to sustain high operating temperature especially using in embedded capacitor application. As a result, in this study, high T_g epoxy composites has been used for fabrication of dielectric material.

Therefore, there are three main problem statements in this study which is the cost of filler materials, poor dispersion of the fillers and T_g of the epoxy. In order to solve the cost of materials, $CaCO_3$ is introduced in this study to save cost and MWCNT is used to achieve higher dielectric constant of the dielectric material. Besides that, functionalization of the fillers such as surfactant and silane coupling agent are introduced in this study to improve the dispersion of the fillers. Lastly, high

T_g of the epoxy which is OP 392 epoxy is used as epoxy matrix for dielectric material in the last section of the works.

1.3 Research Objectives

The objectives of this study are as follows:

i. To compare the effect of particle size of mineral $CaCO_3$ and precipitated $CaCO_3$ on the properties of epoxy thin film composites.
ii. To investigate the effect of various types of nanofiller (precipitated $CaCO_3$, $BaTiO_3$ and MWCNT) and filler loadings on the epoxy thin film composites.
iii. To study the effect of different types of functionalization method on the properties of MWCNT filled epoxy thin film composites.
iv. To determine suitable epoxy resin for fabrication of epoxy thin film composites on embedded capacitor applications.

1.4 Scope of Study

In this study, filler loading of micron size filler (mineral $CaCO_3$) is 0, 5, 10, 15 and 20 vol%, whereas filler loading of nano size filler (precipitated $CaCO_3$, $BaTiO_3$ and MWCNT) is 0, 0.5, 1.0, 1.5 and 2.0 vol%. First, composites with different particle size of mineral $CaCO_3$ and precipitated $CaCO_3$ have been tested to determine the effect particle size on the properties of epoxy thin film composites. Then, various types of filler which are precipitated $CaCO_3$, $BaTiO_3$ and MWCNT have been studied to determine the effect of filler types on the properties of epoxy thin film composite. Besides that, functionalization of MWCNT which are polyoxyethylene octyl phenyl ether (Triton X-100), sodium dodecyl sulfate (SDS) and 3-(aminopropyl)triethoxysilane (AMPTES) are prepared and composites with filler loading of 0, 0.5, 1.0 and 1.5 vol% were evaluated. Then two different types of epoxy composites which are DER 332 epoxy composites and OP 392 epoxy composites are compared in this study. Besides that, various characterization techniques are employed to determine the properties of epoxy thin film composites such as dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), thermogravimetric analysis (TGA) and etc. Dielectric properties, mechanical properties and thermal properties were used to evaluate the performance of the composite materials.

1.5 Organization of Thesis

Fabrication and characterization of epoxy thin film composites as dielectric materials are reported in the thesis. This thesis consists of five chapter. Chapter 1 gives brief introduction on dielectric materials based on polymer thin film composites for embedded capacitor application. This chapter also includes problem statement and research objectives of the present study.

Chapter 2 reports on the literature review which is discussed on capacitor, including types of capacitor, embedded capacitor application and fabrication of embedded capacitor. This chapter also discusses on polymer composites, types of filler, functionalization of filler and properties of dielectric materials. At the end of this chapter, previous works of dielectric materials on embedded capacitor application are included to give brief information about the application of embedded capacitor in recent electronic industry.

Chapter 3 covers the materials and chemicals that are used in this research. This chapter also includes the methodology, experimental procedure of fabricating epoxy thin film composites and characterization.

Chapter 4 discusses on the results which separated into four parts. The first part discussed on the properties of mineral $CaCO_3$ and precipitated $CaCO_3$ filled epoxy thin film composites with different filler loading. The filler loadings used for mineral $CaCO_3$ (micron size) are 0, 5, 10, 15 and 20 vol%, whereas for precipitated $CaCO_3$ (nano size), the filler loading are 0, 0.5, 1.0, 1.5, 2.0 vol%. The second part discussed on the properties of various types of filler which are precipitated $CaCO_3$, $BaTiO_3$ and MWCNT filled epoxy thin film composites with different filler loading (0, 0.5, 1.0, 1.5, 2.0 vol%.). In the third part, the effect of functionalization towards the properties of MWCNT filled epoxy thin film composites with different types of functionalization (Triton X-100, SDS and AMPTES) are reported. In the last part, the comparison properties of epoxies (DER 332 and OP 392) with treated and untreated MWCNT are discussed. Lastly, Chapter 5 reports conclusion of the research and recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Capacitor

Capacitor consists of two conducting layer/plate are separated by insulator layer which known as dielectric. The insulator layer can be nonconducting material whereas the conducting layer can be metal or conductive material. Capacitance (C) is defined as the amount of charge (Q) can be stored on the applied voltage (V).

$$C = \frac{Q}{V} \tag{2.1}$$

The unit of capacitance is farad. Larger value of C means more charge can store for a given voltage (Robbins & Miller, 2004; Bennett, 2011). In normal state, the conducting plate contains free electrons throughout the plate. When dc source is connected, the electrons flow from top conducting plate to bottom conducting plate in the direction of positive potential of battery which shown in Figure 2.1. At that time, the amount of electrons flow from top conducting plate is deposited on the bottom of the plate**.** This is because the presence of the dielectric layer becomes obstacle to block the electrons flow from bottom plate to top plate. As a result, top conducting plate becomes positively charged and bottom conducting plate becomes negatively charged (Robbins & Miller, 2004). When the capacitor's charge capability is reached, the capacitor is fully charged at this stage where it stops to accept the electrons from the circuit. Figure 2.1 shows the schematic capacitor under an applied of electric field (Bennett, 2011).

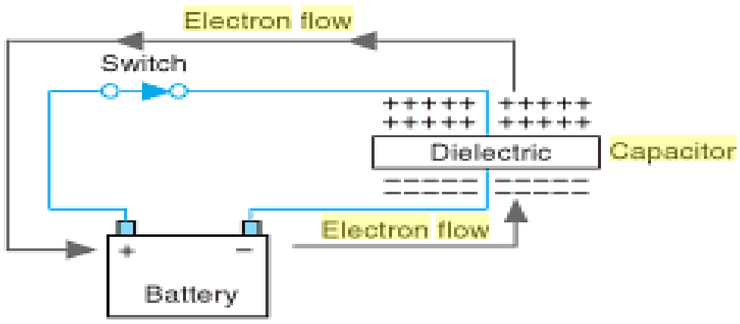

Figure 2.1: The set up of capacitor in the presence of an applied electric field (Bennett, 2011).

When the dc source is disconnected, the excess electrons which are deposited at bottom plate move back to the top plate of the conducting layer. In this stage, the capacitor is said to be discharged and current still flow due to mobility of the electron. Once all the electrons is move back to the top plate and no further movement of electron, the current is no longer flow and thus zero (Robbins & Miller, 2004).

2.1.1 Types of Capacitor

There are varieties of capacitor available in commercial market. Common commercial capacitors are electrolytic capacitor, film capacitor, ceramic capacitor, mica capacitor and others that can be found in the market place (Glisson, 2011; Linsley, 2013). Figure 2.2 shows the various type of discrete capacitor that available in commercial market. Different capacitors are used in different electronic application. Film capacitor for example is made by polymer materials such as polyester that form several layer of the film to form a discrete capacitor. Even though film capacitor has good electrical and thermal properties, but it is not suitable to use in high frequency application (Linsley, 2013). Meanwhile for electrolytic capacitor, a dielectric layer is consists of thin oxide layer that used in large value of capacitance (Glisson, 2011).

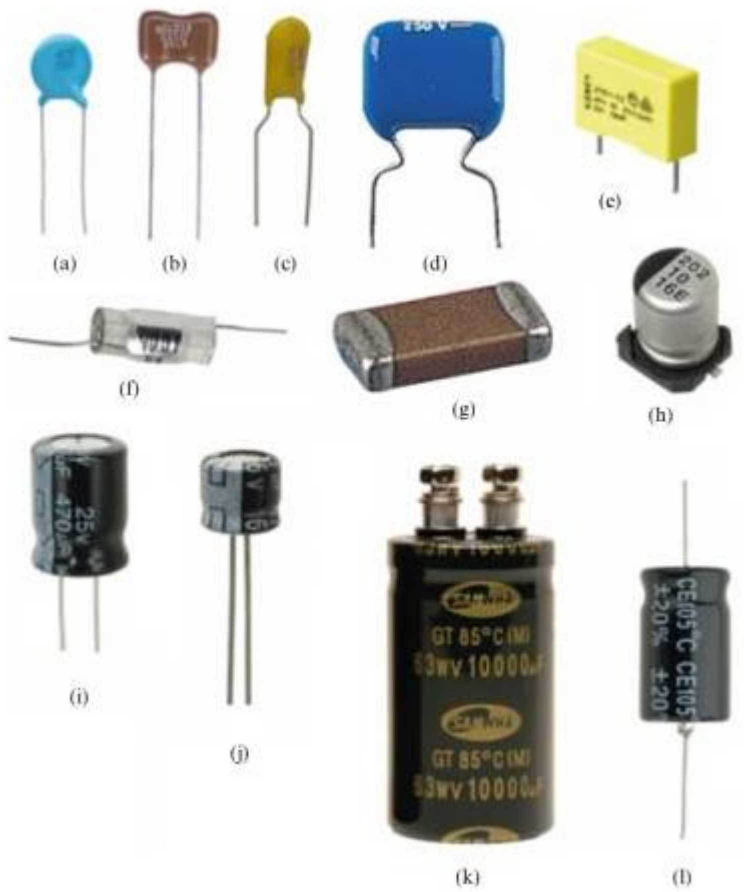

Figure 2.2: Different type of discrete capacitors (a) ceramic (b) mica (c) tantalum (d), (e) polypropylene (f) polystyrene (g) ceramic chip (h-l) electrolytic capacitor (Linsley, 2013).

In other hand, embedded capacitor is another type of capacitor that can be used to replace discrete capacitor. According to previous report by Peiffer (2001), it was reported that embedded capacitor that printed on printed circuit board (PCB) board is used to replace the usage of discrete capacitor. It consists of thin dielectric material that embedded into PCB on electronic package. Meanwhile, many previous researchers such as Cho *et al.* (2004), Hwu *et al.* (2005) and Lu *et al.* (2007) have studied on embedded capacitor application. They usually used high dielectric constant filler such as barium titanate to fabricate embedded capacitor material. As a result, it has been proved that embedded capacitor application has become popular in recent industry research.

2.1.2 Embedded Capacitor Application

Embedded capacitors are capacitor where it can be in thin film that laminated and embedded inside a PCB (Peiffer, 2001). The embedded capacitor consists of thin dielectric material sandwiched between two conductive elements. The dielectric material usually has high dielectric constant and low dielectric loss insulator which enhances storage of charge whereas for conductive material, it functions as power and ground plane. Figure 2.3 shows the set-up of embedded capacitor thin film is laminated inside PCB (Alam *et al.*, 2011).

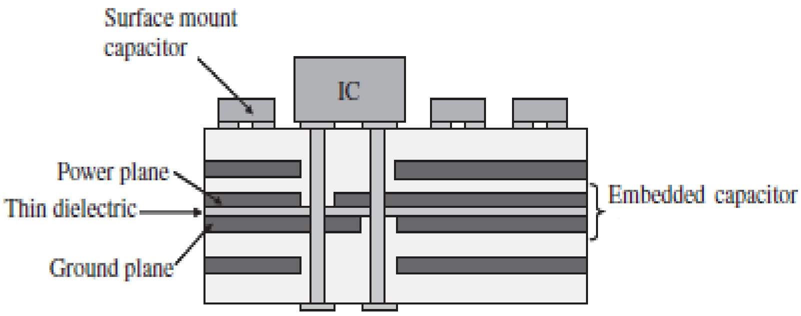

Figure 2.3: Embedded capacitor application (Alam *et al.*, 2011).

Renaule & Munier (2012) fabricated five dimensions square shape dielectric layers which were 1 mm^2, 9 mm^2, 1 cm^2, 9 cm^2, 100 cm^2. These dielectric layers embedded in the PCB board which contained two copper electrodes between them. Figure 2.4 shows the lay-up of PCB with embedded capacitor that green colour represents substrate, orange colour represent copper and grey colour represent dielectric material (Renaule & Munier, 2012).

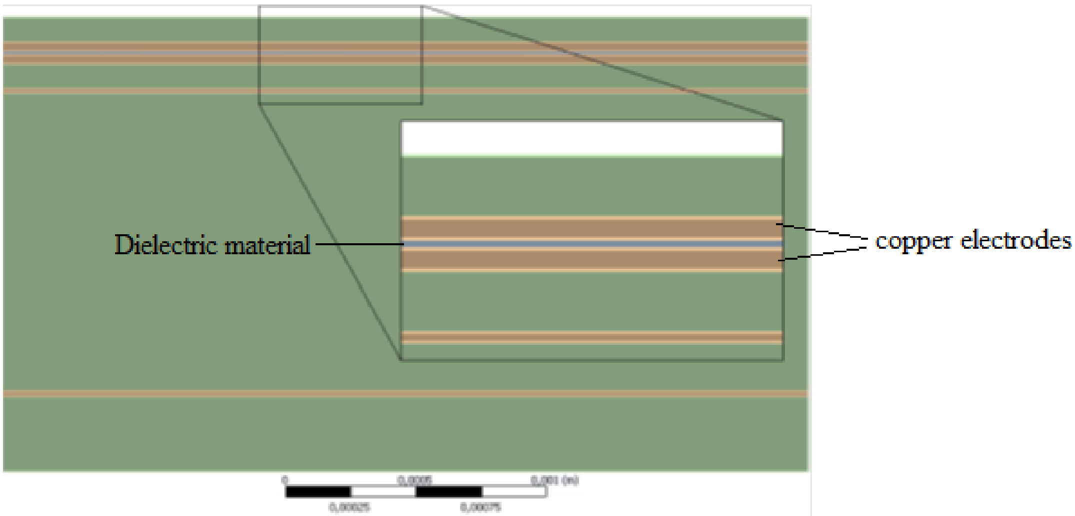

Figure 2.4: Lay up of embedded capacitor with PCB (Renaule & Munier, 2012).

2.1.3 Fabrication of Embedded Capacitor

Many researchers have used different methods to fabricate embedded capacitor. According to Peiffer (2001), the dielectric thickness should be as thin as possible to increase the capacitance value. In previous works, many researchers have used polymer film composites as dielectric material of embedded capacitor application. Cho *et al.* (2004) have used common roll coated which shown in Figure 2.5 where the polymer solution was coated on a releasing film. Goyal *et al.* (2013) have used hot press technique where polymer film was undergoing hot press at the heating rate of 4 ^{0}C/min under pressure of 45 Mpa. Luo *et al.* (2009) have used bar coating method to form embedded capacitor film. Besides that, there are several methods such as hand layout technique, dipping technique, spin coating method to produce polymer film for embedded capacitor application.

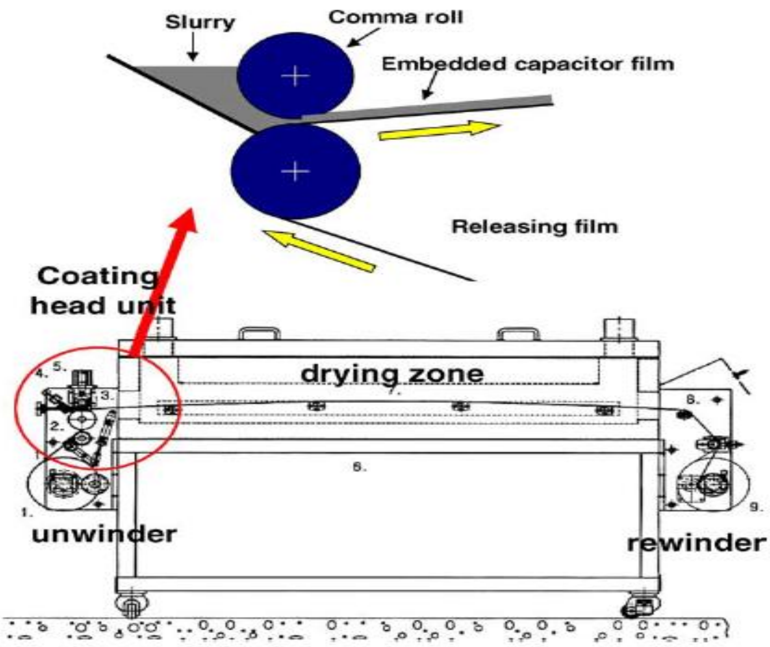

Figure 2.5: Formation of embedded capacitor film by using common roll coated (Cho *et al.*, 2004).

2.1.3.1 Spin Coating Process

Spin coating process, it is a common technique that used to produce a thin and smooth film on the flat substrates. It can apply to many types of polymer solution to be coated on the disc flat substrates. The thickness of the film depends on spin speed, the volatility of the solvent and the viscosity of the polymer solution. There are several stages of spin coating process which is deposition, spin up, stable fluid outflow and evaporation which shown in Figure 2.6 (Michler, 2008).

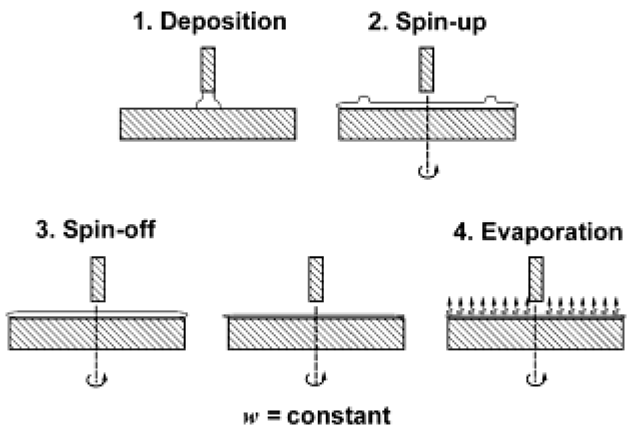

Figure 2.6: Spin coating process of polymer solution to produce thin film layer (Michler, 2008).

First the polymer solution deposited on the disk shape flat substrate. The disk will rotate slowly to start phase of the spin coating process where the centrifugal force will cause the liquid from the centre flow outwards across the entire disk. Then the substrate will spin up to high rotation rate (rpm). This is because rotating with high speed will cause the polymer solution flow radially due to centrifugal force and able to cover the substrate completely. At the spin off phase, the film of the polymer solution will form very thin uniform film and the excess of the polymer solution is ejected from the edge of the disc substrate. If the polymer solution contains the remaining solvent, the solvent will be evaporated. The spin coating process is completed by evaporating all the remaining solvent (Michler, 2008).

The thickness of the film depends on spin speed, the volatility of the solvent and the viscosity of the polymer solution (Michler, 2008). According to Smirnov *et al.* (2010), the thickness of film decreased with increasing the speed rotation. This is because high speed produces high centrifugal force that the polymer solution flow radially (Michler, 2008). Besides that, high viscous of polymer solution produces thicker film composites due to high viscous polymer solution lower the shear rate of solution near the center of the disk shape flat substrate.

2.2 Polymer Composites

Composite material is the combination of two or more materials that can be formed to achieve superior properties. The main components of composite materials are fiber and matrix. The matrix such as polymer is usually ductile and provides better toughness whereas for the fiber, it can be known as filler that usually reinforce the matrix phase and provides stiffness and strength for composites (Barbero, 2011; Thomas *et al.*, 2012). Nowadays composites materials become essential part of material due to low weight, corrosion resistance, high fatigue strength and save cost (Thomas *et al.*, 2012). These composites material can be used in aircraft structure, electronic application and medical application (Thomas *et al.*, 2012).

Various polymer composite materials have been studied in past few years for embedded capacitor application (Cho *et al.*, 2004; Kakimoto *et al.*, 2006). Many researchers have used polymer ceramic composite to produce dielectric material for embedded capacitor application. This is due to polymer matrix has low processing temperature and flexibility while ceramic fillers have high dielectric constant (Cho *et al.*, 2004; Kakimoto *et al.*, 2006; Lu *et al.*, 2007). As a result, combination of ceramic and polymer is recommended as dielectric material which enhances storage of charge to achieve high dielectric constant and low processing temperature (Alam *et al.*, 2011). In previous research, polymer matrices such as epoxy, Polymethyl methacrylate (PMMA), polyimide, Polytetrafluoroethylene (PTFE) and ceramic fillers such as barium titanate, barium strontium titanate, lead zirconate titanate have been studied (Cho *et al.*, 2004; Goyal *et al.*, 2013; Stefanescu *et al.*, 2001; Alias, 2012; Kim *et al.*, 2011; Wu *et al.*, 2009).

In previous work, there are several methods to produce polymer composites for embedded capacitor application. Hwu *et al.* (2005) prepared ERL 4221 epoxy/ barium titanate composite with dispersion agent and ball mill for 24 hours at 300 rpm to ensure good dispersion. Cho *et al.* (2004) have mixed $BaTi0_3$ powders, dispersant and solvent with epoxy and hardener by using ultrasonication to break down the agglomeration. Goyal *et al.* (2013) in that study considered PMMA and BT powders where the materials were mixed together with chloroform by using ultasonication and further stirred and heated to produce a viscous solution.

Instead of using polymer ceramic composites, conductive filler filled polymer composites are another approach towards high dielectric constant material for embedded capacitor application (Lu & Wong, 2008). In previous research, conductive filler such as carbon nanotube (CNT), silver (Ag) and aluminium (Al) have been studied for capacitor application. Rao & Wong (2002) prepared silver/epoxy composite for capacitor application. Epoxy mixture mixed with 7.38 vol% to 20.69 vol% silver loading until the homogeneous paste was formed. Xu & Wong (2003) and Chen *et al.* (2009) have prepared aluminium filled epoxy composite mixture. The aluminium powder mixed with epoxy solution by using manual stiring, ultrasonication mixing and high shear blend to achieve better dispersion.

Polymer composites can be produced in the form of thin film composites which are widely used in electronic application such as sensor, solar panel and touch panel (Foo *et al.*, 2011). In previous work, researchers have study on fabrication of thin film composites as dielectric materials for embedded capacitor application (Peiffer, 2001; Cho *et al.*, 2004). They found out that the thin film composite provides superior properties such as mechanical, thermal and electrical properties with low demand of materials (Foo *et al.,* 2011; Saw *et al.*, 2012). As a result, the fabrication of thin film composite not only can reduce the manufacturing cost but it also suitable to be used in embedded capacitor application as electronic device tend to be designed in thinner form (Cho *et al.*, 2004).

2.3 Epoxy

In previous research, many researchers have studied on epoxy composites to form dielectric materials for embedded capacitor application (Cho *et al.*, 2004; Yoon *et al.*, 2009; Alam *et al.*, 2011; Luo *et al.*, 2009; Wu *et al.*, 2009). Epoxy is thermosetting polymer which contains epoxide, ethoxylene or oxirane functional group which is known as epoxy group. Generally epoxy group contains epoxy ring which consists of two carbon atoms bonded with one oxygen atom (Tummala *et al.*, 1997).

To produce epoxy thermoset, it requires hardener (curing agent) to crosslink with epoxy resin (Pascault & Williams, 2010). Epoxy resin can be cured by amine hardener which contains -NH bond to crosslink with epoxy resin (Tummala *et al.*, 1997; Brock *et al.*, 2000; Rowel, 2012; Hoa, 2009). These materials can be chosen as hardener of epoxy due to it contains active hydrogen that attacks the terminal carbon of epoxy with hydrogen atom which is shown in Figure 2.7 (Rowel, 2012; Tummala *et al.*, 1997). The active hydrogen interacts with oxygen atom and open epoxy ring for crosslinking reaction (Rowel, 2012).

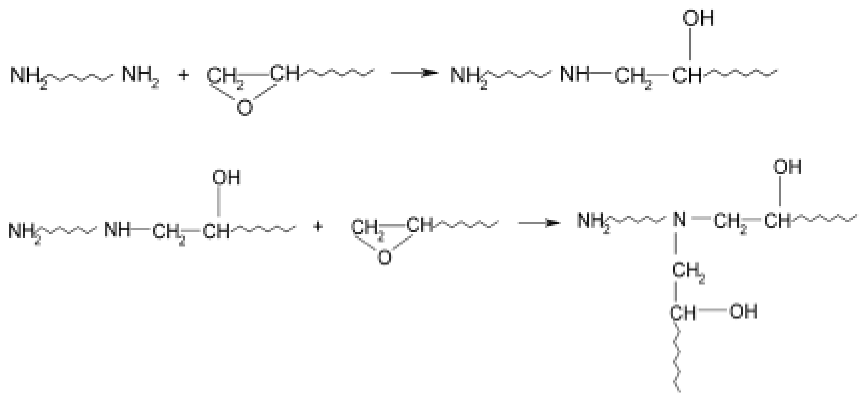

Figure 2.7: Schematic reaction between amine hardener with epoxy resin (Hoa, 2009).

2.4 Filler

Previous common research on embedded capacitor application has been considered ceramic filler filled polymer composites as dielectric material (Cho *et al.*, 2004; Hwu *et al.*, 2005; Yoon *et al.*, 2009; Luo *et al.*, 2009). Wu *et al.* (2009) reported that dielectric constant increased from 5 to 23.6 at 1 MHz when the content of Barium Strontium Titanate Zirconium (BSTZ) increased from 10 wt% to 70 wt% with epoxy matrix. This is because the unique properties of ferroelectric ceramic filler provide high polarization which give high dielectric constant for polymer composite and enhanced the capacitance of the film (Wang, 2002).

Besides that, conductive filler filled polymer composite has been studied for embedded capacitor application due to dielectric constant of composite increased with increasing conductive filler loading (Xu & Wong, 2003; Rao & Wong, 2002). According to Xu & Wong (2003), the maximum dielectric constant was 109 for 80 wt% of 10 µm aluminium and 60 for 50 wt% of 100 nm aluminium. According to

Rao & Wong (2002), the dielectric constant of silver/epoxy composite was 200 at 11.03 vol% of flake silver. As a result, it has proved that conductive filler provides better dielectric constant value compared to the ceramic filler.

2.4.1 Calcium Carbonate ($CaCO_3$)

Calcium carbonate ($CaCO_3$) can be used as filler for polymer due to low cost and locally available material. The mineral $CaCO_3$ can be produced by different mineral sources such as chalk, limestone and marble. Limestone, the backbone of $CaCO_3$ industry, exists in abundant quantities in the form of large mineral deposits found in Kuala Lumpur, Selangor, Perak and Perlis. The existence of a huge deposit of limestone around Ipoh where Perak is the major producer of $CaCO_3$ powder in Malaysia (Junin & Mustapha, 1988). The main reason of using mineral $CaCO_3$ as filler is for price reduction and improves mechanical and thermal properties of composites (D'Haese et al., 2011).

Precipitated $CaCO_3$ is known as purified, refined or synthetic $CaCO_3$. Equation 2.2, 2.3 and 2.4 show the reaction of precipitated $CaCO_3$. Precipitated $CaCO_3$ is formed by heating limestone to calcite oxide (CaO) at temperature range of 600^0C-900^0C. Next the calcite oxide will react with water to produce calcium hydroxide ($Ca(OH)_2$). Then the calcium hydroxide will react with carbon dioxide when the limestone is calcined to produce calcium carbonate and water. Lastly, the precipitated calcium carbonate is separated by water through filtration and various other separation method (Myers, 2007).

$$CaCO_3 \rightarrow CaO + CO \quad (2.2)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2.3)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (2.4)$$

Generally, commercial $CaCO_3$ can be divided into two forms which are mineral $CaCO_3$ and precipitated $CaCO_3$. Compared to mineral $CaCO_3$, precipitated $CaCO_3$ possesses a smaller particle size and, thus gives higher reinforcement. Particle size of precipitated $CaCO_3$ can be reduced in the nanoscale, has been produced and commercialized. It has been found that nano size of precipitated $CaCO_3$ play important roles in the strengthening of polymer composites due to homogenous dispersion of nanoparticles inside a polymer matrix (Khan & Bhat, 2014). According to Mishra and Shimpi (2005), tensile strength of precipitated $CaCO_3$ nanocomposites which was 2.5 MPa was higher compared to the commercial $CaCO_3$ which was 1.3 MPa. As a result, good dispersion of nanoparticles provides greater reinforcement of composite systems (Khan & Bhat, 2014).

2.4.2 Barium titanate ($BaTiO_3$)

Barium titanate ($BaTiO_3$) is one of the ceramic filler that frequently used to produce dielectric material for embedded capacitor application (Cho *et al.*, 2004; Goyal *et al.*, 2013; Kim *et al.*, 2011). Perovskite ceramic material consists of ternary compound (ABO_3) where A and B cations have different atomic size respectively. The structure of barium titanate ($BaTiO_3$) consists a combination of a large Ba^{2+} (A) cation and oxygen to form FCC lattice and small Ti^{4+} (B) cation occupies the interstitial sites in FCC array. This structure is known as perovskite structure which plays an important role in dielectric properties. Figure 2.8 shows the perovskite structure of $BaTiO_3$ (Wang, 2002).

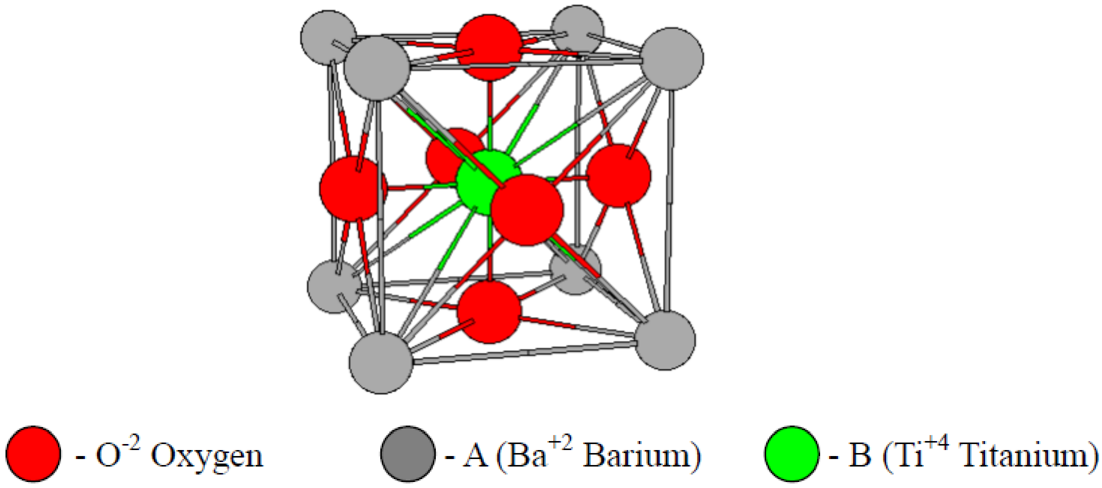

Figure 2.8 : Perovskite structure of Barium Titinate (Wang, 2002).

Perovskite $BaTiO_3$ exhibits dielectric, ferrorelectric and piezoelectric properties. Ferrorelectricity of $BaTiO_3$ provides spontaneous dipole moment which can be switched by the application of electric field. $BaTiO_3$ exhibits nonlinear dielectric properties and has high dielectric constant (Barsoum, 2003). The ferroelectric properties with high dielectric constant makes $BaTiO_3$ is a best choice for many electrical application such as thermistors, multilayer capacitors (MLCs) and energy storage devices (Wang, 2002). When temperature of $BaTiO_3$ above Curie temperature (120 ^{0}C), it exhibits non-ferroelectricity where no electric dipole exists in the material (Barsoum, 2003).

In previous research, dielectric properties increased with increasing ceramics filler loading. Luo *et al.* (2009) reported maximum dielectric constant of 50 vol% barium titanate filled epoxy composite was 19.4 at 10 kHz. According to Cho *et al.*

(2004), the maximum dielectric constant of barium/epoxy composite at 60-65 vol% was 57. However, according to Yoon *et al.* (2009), ceramics filler loading should not exceed 50 vol% due to poor interaction between polymer and ceramics filler. This is because when the ceramics loading increased, the viscosity of the polymer composite increased and cause difficulty in mixing. Besides that, poor interaction of $BaTiO_3$ cause existing of voids and pores which affects the dielectric properties of the composite system (Cho *et al.*, 2004; Luo *et al.*, 2009).

2.4.3 Carbon Nanotube (CNT)

Many researchers recently have studied on carbon nanotube (CNT) for various application due to CNT has unique properties especially in electrical and mechanical properties (Park *et al.*, 2008; Guo *et al.*, 2006; Ma *et al.*, 2010; Li *et al.*, 2008a). CNT consists of graphene sheet which it has been rolled up into cylinder (Chen & Zhang. 2009; Li *et al.*, 2008a). There are two types of CNT which is single wall carbon nanotube (SWCNT) and multiwall carbon nanotube (MWCNT). SWCNT consists of single graphene layer rolled into cylinder whereas MWCNT consists of two or more graphene sheet form concentric cylindrical shell around a central hollow core (Ma *et al.*, 2010). The carbon atom is arranged in hexagonal lattice which it contains three nearest atom with a distance of 0.144 nm along the bond that are separated by 120^0 (Chen & Zhang, 2009). CNT has high electrical properties due to delocalized π bond across nanotube which leads to electronic properties of nanotube (Francois Leonard, 2009).

Many researchers have found that CNT can enhance dielectric properties such as dielectric constant of polymer composites. According to Chang *et al.* (2012), as the content of CNT increased, the distance between CNT decreased and maximum amount of microcapacitors is achieved. Li *et al.* (2008b) proved that the largest dielectric constant of MWCNT/PVDF was 1700 when 6 vol% of MWCNT was added at 1 kHz.

Besides that, the presence of CNT reinforced with polymer matrix to provide good mechanical properties. Many researchers have found that CNT becomes essential in structural application due to unique atomic structures. The bond strength of C-C of MWCNT provides outstanding mechanical properties (Husaen, 2012; Gkikas *et al.*, 2012). According to Husaen (2012), tensile strength and tensile modulus of 0.1 wt% CNT/epoxy was 72 MPa and 48 MPa, respectively which was improved by 243 % and 508 %, respectively compared to the neat epoxy. However high content of CNT in epoxy resin gives poor dispersion that deteriorates mechanical properties of the composites systems (Cheng *et al.*, 2008).

2.5 Ultrasonication

The properties of composites depend on dispersion state and homogeneity of nanoparticle. There are various techniques to improve dispersion state of nanoparticle throughout polymer matrix. Ultrasonication is one of the technique that nanoparticle can dispersed effectively well into polymer matrix by ultrasonic wave. In order to achieve uniform dispersion, the probe sonicator of ultrasonication is used to break the cluster in the matrix. The mechanical dispersion of filler is carried out to disentangle filler such as CNT from each other by vibration energy or shear force (Geng *et al.*, 2008a).

Ultrasonication is applying ultrasound energy to agitate particles in a solution. The probe sonicator is usually made by inert metal such as titanium and have an adjustable amplitude vary from 20 % to 70 % and a power of 100-1500 W. When ultrasound energy propagates, it produces the waves that passing through the solution and induced in the molecules of the medium where it separates the individualized nanoparticle from the bundle. Low viscosity of liquid gives better dispersion for filler to disperse compare to high viscosity of liquid. Besides that, during sonication mixing, the sample of the mixture should be kept cold by using cool water bath and sonication must be done in short intervals due to consequence of sonication generates heat (Pastore,2012).

However long sonication time and high input energy cause filler damage and deteriorate the properties of filler (Geng *et al.*, 2008a). Lu *et al.* (1996) reported that long sonication treatment cause graphene layer fracture, bending and bucking defect of CNT. This is due to long duration of sonication treatment causes CNT become amorphous and damage occur from external carbon layers to inner layer gradually. At the end, the damaging of carbon nanotube affects the properties of composite (Lu *et al.*, 1996).