THE EFFECT OF MIXING PARAMETERS AND SURFACE TREATMENT ON THE PROPERTIES OF CORDIERITE FILLED POROUS EPOXY

by

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LIST OF ABBREVIATION

3-APE	3-aminopropyltriethoxysilane
AA	Acetic Acid
ASTM	American Society for Testing and Materials
DGEBA	Diglycidyl ether of bisphenol A
EPDM	Ethylene-propylene-diene monomer
EVA	Ethylene-vinyl acetate
FTIR	Fourier transform infrared
MWNTs	Multi-walled carbon nanotubes
NBR	Poly (acrylonitrile – co – butadiene)
SEM	Scanning electron microscopy
T_g	Glass transition temperature
T_m	Melting temperature
TGA	Thermal gravimetric analysis
XRD	X – ray diffraction

LIST OF SYMBOL

GPa	Giga pascal
°C	Degree celsius
%	Percentage
SiO_2	Silicon dioxide
$Mg_3Si_4O_{10}(OH)_2$	Magnesium silicate
$Al_3O_3.2SiO_2.2H_2O$	Kaolinite
Al2O3	Aluminum oxide
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	Cordierite
NaOH	Sodium hydroxide
H_2O	Water
g/cm^3	Gram per cubic centimeter
cP	Centipoise
µm	Micron
g/mol	Grams per mole
vol%	Volume percent
wt%	Weight percent
mm	Millimeter
°C/ min	Degree Celsius per minute
ε'	Dielectric constant
MPa	Mega pascal
T_g	Glass transition temperature
kHz	Kilo hertz
MHz	Mega hertz

KESAN PARAMETER PENCAMPURAN DAN PERAWATAN PERMUKAAN TERHADAP EPOKSI TERLIANG TERISI KORDERIT

ABSTRAK

Apabila kelajuan pemprosesan komponen elektronik meningkat dengan kemajuan teknologi, prestasi keseluruhan sistem yang digunakan adalah terikat lengah perambatan dalam saling berhubung , manakala kelajuan perambatan isyarat dalam saling hubungan adalah bergantung kepada bahan dielektrik. Bahan-bahan dielektrik semasa seperti polyimide padat mempunyai pemalar dielektrik 3.2. Generasi akan datang peranti elektronik memerlukan bahan yang mempunyai pemalar dielektrik di bawah 3. Untuk meningkatkan kelajuan perambatan isyarat dan mengurangkan lengah perambatan , nilai dielektik yang rendah telah dibangunkan. Kajian ke atas epoksi terliang terisi korderit adalah terdiri dari empat bahagian. Bahagian pertama kajian ini melibatkan pengkajian mengenai kesan urutan pencampuran terhadap : epoksi, latek kemudian bahan pengeras (ELH) dan epoksi, bahan pengeras kemudian latek (EHL) melalui pengekstrakan getah asli latek menggunakan air dan tolena sebagai medium pengekstrakan yang dibandingkan antara teknik ultrasonic dan tanpa ultrasonic. Epoksi terliang terhasil selepas pengekstrakan getah asli latek di dalam system pencampuran epoksi dan latek. Pencampuran antara epoksi/latek disediakan menggunakan teknik pencampuran mekanikal pada suhu bilik dan dan kelajuan pemutar 400rpm. Kandungan latek telah diubah dari 0.5 sehingga 2.0 phr. Epoksi terliang yang terhasil dari pengekstrakan menggunakan tolena dengan teknik ultrasonic menunjukkan nilai ketumpatan yang rendah seperti yang dijangka. Lebih banyak struktur terliang dalam epoksi menyebabkan penurunan nilai pemalar dielektrik yang diaplikasikan dalam pembungkusan elektronik.Walau bagaimanapun kekuatan dan modulus pelenturan berkurang.Kajian bahagian kedua dijalankan menggunakan ammonia dan asid asetik untuk membandingkan kepekatan latek.Di dapati bahawa kepekatan memainkan peranan yang penting dalam menghasilkan lebih banyak struktur terliang. Latek dengan nilai pH 11 dipilih untuk pencampuran epoksi, latek dan bahan pengeras kerana menghasilkan nilai pemarar dielektrik yang rendah. Korderit telah disentesiskan dalam bahagian ketiga kajian ini yang digunakan sebagai pengisi terhadap epoksi terliang. Di sini korderit telah dipilih kerana mempunyai kekuatan yang tinggi. Kandungan korderit telah diubah dari 2.5 hingga 10% isipadu. Epoksi terliang terisi korderit menunjukkan lenturan yang lebih baik, haba dan pemalar dielektrik yang setara jika dibandingkan dengan tanpa korderit. Perbandingan kajian antara epoksi terliang terisi korderit yang melibatkan penggunaan agen pengkupil silana dan tanpa menggunakan agen pengkupil silana dijalankan dalam bahagian ke empat kajian. Keputusan kajian menunjukkan korderit yang dirawat menggunakan silana menunjukkan pengurangan nilai pemalar dielektrik dan meningkatkan sifat-sifat mekanikal. Dalam kajian yang keempat, kandungan korderit yang optimum dipilih untuk untuk dilakukan rawatan permukaan menggunakan 3-Aminoprophyltrimetiloxysilane (3APE) untuk membentuk kumpulan berfungsi pada permukaan korderit dalam matrik epoksi tunggal. Kumpulan berfungsi digabungkan atas permukaan kerderit telah dikesan oleh Spektroskopi Fourier Transform Infra Merah (FTIR). Morfologi permukaan patah selepas ujian lenturan dikaji dengan Mikroskopi Penskanan Elektron (SEM). Hasilnya menunjukkan interaksi

antara korderit dan matriks epoksi bertambah baik selepas rawatan permukaan korderit. Tambahan pula didapati bahawa kekuatan lenturan dan modulus komposit bertambah selepas rawatan permukaan korderit dilakukan. Di samping itu, kestabilan terma telah meningkat selepas rawatan permukaan dilakukan dimana suu penguraian epoksi terliang terisi korderit terawatt permukaan lebih tinggi berbanding korderit yang tidak dirawat. Tambahan pula, didapati bahawa nilai pemalar dielektrik berkurang selepas rawatan permukaan. Nilai pemalar dielektrk telah dicapai dan meningkatkan sifat-sifat mekanikal. Pengunaan lapisan dielektrik yang baru dalam bahan substrat boleh membantu untuk meningkatkan kelajuan litar berbanding polyimide tanpa liang.

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ABSTRACT

As the processing speed of the electronic components increased with technology advances, the overall performance of the system is limited by the propagation delay in the interconnections, while the propagation speed of signal in interconnections is depended on the dielectric materials. The current dielectric materials such as dense polyimide have dielectric constant of 3.2. Future generation of electronic devices require the material to have dielectric constant below 3. To increase signal propagation speed and reduce propagation delay, low dielectric constant material has to be developed. The research on porous epoxy filled with cordierite consists of four parts. The first part of the study was to investigate the effect of mixing sequences: epoxy, latex then hardener (ELH) and epoxy, hardener then latex (EHL) through the extraction of NR latex using water and toluene as extraction medium were compared between ultrasonic and without ultrasonic technique. Porous epoxy was obtained after the extraction of NR latex in the mixture of immiscible system of epoxy/latex blending. The mixing of epoxy/latex was prepared by mechanical mixing stirrer at room temperature and rotor speed of 400rpm. The latex content was varied from 0.5 to 2.0 phr. As expected, the density result showed lower values in the porous epoxy extracted by toluene with ultrasonic technique. More porous structure in epoxy leaded to lower value in dielectric constant which prefer for dielectric layer in substrate material. However, it also caused a decrease in flexural strength and modulus. The second part of research was carried out the modification of the viscosity of latex using ammonia and acetic acid. It was found that the viscosity of latex plays the important parameter to produce more porous structure. Optimum pH value was selected at 11 using epoxy, latex then hardener (ELH) mixing sequences due to the lowest dielectric constant value. Cordierite was synthesized in the third part of the study. It was used as the filler in porous epoxy. Cordierite was chosen here due to its high strength and modulus properties. The cordierite content was varied from 2.5 to 10 volume %. The cordierite filled porous epoxy showed better flexural strength and dielectric constant properties than without filler loading. On the other hand, thermal stability was increased with increasing in cordierite content. In the fourth part of study, the optimum content of the cordierite was treated with 3-Aminoprophyloxysilane (3-APE) in order to form surface functional group on cordierite surface in epoxy matrix. The functional group grafted on the surface of cordierite was detected by Fourier Transform Infrared Red (FTIR). The morphology of fracture surface after flexural test was observed by Scanning Electron Microscopy (SEM). The results showed the interaction between cordierite and epoxy matrix was improved after surface treatment of cordierite. It was found that the flexural strength and modulus of porous epoxy increased after the surface treatment. On the other hand, the thermal stability was also improved with the surface treated cordierite in which the decomposition temperature of porous epoxy with treated cordierite was higher than the porous epoxy with untreated cordierite. Furthermore it was found that the dielectric constant value was reduced after surface treatment. A dielectric constant of 2.8 was achieved with increasing the mechanical properties. Usage of this new low dielectric

material as dielectric layer in substrate materials can help to improve circuit speed compared to the dense polyimide.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The development of low dielectric constant materials helps to improve the performance of microelectronic devices. The dielectric constant of the dielectric layer effects the signal propagation delay time and cross-talk in the interconnects. Therefore, a low dielectric constant is required for the dielectric layer to improve device performance. A number of low-k materials have been studied for use as interlayer dielectric. To further lower the dielectric constant, researches directed the development of low-k materials on replacing the solid materials with air, whose dielectric constant is closed to 1. This creates need for developing novel technique for the manufacturing of porous material especially porous polymers (Ho et al., 2003).

Recent studies had explored and obtained several intrinsic low dielectric constant polyimides with outstanding comprehensive properties by molecular design via introducing some rigid non planar conjugated structures, like triphenylethylene or tetraphenylethylene, into the polyimide backbone (Chen et al., 2016). Herein, another sterically hindered and nonpolar bulky group, triphenylmethane, were introduced into the structure of two novel aromatic diamine monomers TriPMPDA and TriPMMDA, followed by fabricating the corresponding polyimide films with dianhydride 6FDA via conventional two-step polymerization. The resulting polyimides exhibited low dielectric with value of 3.2 and highly organosoluble properties with good thermal stability and favorable mechanical properties.

Epoxy resins are usually used as insulating and structural materials in manufacturing microelectronic devices and components such as computer chip packaging and circuit boards (Guo et al., 2008). The epoxy system was selected because it's good thermal and dimensional stability, excellent chemical and corrosion resistance, and superior mechanical and electrical properties (Dai et al., 2010). Porous epoxy thermosets can reduces the dielectric constant by substitution of a portion of the matrix material with air. Reduced size in microelectronics has created a need for porosity at the nanometer scale in materials.

There are many ways to create porous structure in epoxy. One other possible approach is to create a two phase mixture and remove the minority phase through extraction method. This is the approach taken in this study through the solvent extraction of immiscible polymer blends. In this study, epoxy resin with amine groups as hardener and natural rubber latex were used to prepare a porous polymer. Latex was used as dispersed phase in the epoxy system during mechanical stirrer mixing. Then, the latex phase was extracted from the blend by a selective solvent (toluene and water), thereby creating the pores in the epoxy system. This study is focused on mixing method and characterizing the latex content in the blend and its effect on the pore structure to reduce the dielectric constant properties.

The only beneficial results of increasing the porosity are realized in lowering of the dielectric constant. From the mechanical point of view, the increase in porosity strongly impacts the stiffness, fracture resistance and interfacial adhesion. Thus by adding some filler it can influence on mechanical properties. Cordierite ($Mg_2Al_4Si_5O_{18}$)

possesses many excellent physical properties in microelectronic applications, such as substrates in hybrid circuit as well as packaging material in electronic packaging. Because cordierite have a low dielectric constant (5- 6 at 1 MHz) close to that of silicon, they are quite attractive to the electronics industry especially for high frequency circuits.

Besides the properties of fillers, the filler matrix interaction also influence on mechanical properties. There are various surface treatment used with the aim to improve the interaction between filler and matrix. Bula and Jesionowski (2007) studied the effect of filler surface modification on silica nanofillers. It was found that filler surface modification determining fine dispersion and homogenous distributions of filler particles in the matrix.

1.2 Problem Statement

Performance improvements in microelectronic integrated circuits (ICs) over the past few decades have, for the most part, been achieved by increasing transistor speed, reducing transistor size, and packing more transistors onto a single chip. Smaller transistor works faster, so ICs have become faster and more complex. An emerging factor that may disrupt this trend is the showing speed of signal propagation within the chip. Signal delays, caused by the interconnection wiring, increase with each generation of scaling and may soon limit the overall performance of the integrated system. Dielectric constant is one of the major factors affecting the performance of the package. It is because dielectric constant plays important role in determining the circuit speed. As known, that the signal transmission from the silicon chip to the board is governed by the dielectric constant of substrate. If the total resistance is low, the signal will be propagate