SODIUM BICARBONATE AS BLOWING AGENT ON MORPHOLOGY AND PROPERTIES OF CONDUCTIVE CARBON BLACK-FILLED EPOXY POROUS PREPARED BY EMULSION SYSTEM

by

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A report submitted in partial fulfilment of the requirements for the degree of Master of Science in Materials Engineering

School of Materials Engineering
UNVERSITI MALAYSIA PERLIS

2017

UNIVERSITI MALAYSIA PERLIS

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Academic Session : 2017

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ACKNOWLEDGEMENT

My deep gratitude goes first to my respectful supervisor, Dr Zunaida Zakaria as a main supervisor and Dr Du Ngoc Uy Lan as a co-supervisor, who expertly guided me throughout the course of this work. Their guidance, suggestion, opinion and willingness in revising the final part of the report are much appreciated. In addition, their unwavering enthusiasm for physics kept me constantly engaged with my research helped make my time enjoyable. My appreciation also extends to my all lab technicians for their help in lab works and discussion. I also would like to thank my friends for their positive support and constructive opinion.

Above ground, I am indebted to my family, whose value to me only grows with age and their support in my life. I am particularly grateful to Education Ministry Malaysia for providing me the financial support.

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LIST OF ABBREVIATIONS

ADC	Azodicarbonamide
ASTM	American Standard for Testing and Materials
CEP	Conductive epoxy porous
CEP-C0	Conductive epoxy porous without carbon black
CEP-C10	Conductive epoxy porous filled 10 phr carbon black
CEP-C20	Conductive epoxy porous filled 20 phr carbon black
CEP-C30	Conductive epoxy porous filled 30 phr carbon black
CEP-C40	Conductive epoxy porous filled 40 phr carbon black
CEP-C50	Conductive epoxy porous filled 50 phr carbon black
CEP-S0	Conductive epoxy porous without sodium bicarbonate
CEP-S4	Conductive epoxy porous filled 4 phr sodium bicarbonate
CEP-S8	Conductive epoxy porous filled 8 phr sodium bicarbonate
CEP-S12	Conductive epoxy porous filled 12 phr sodium bicarbonate
CEP-S16	Conductive epoxy porous filled 16 phr sodium bicarbonate
CEP-S20	Conductive epoxy porous filled 20 phr sodium bicarbonate
CPC	Conductive polymer composite
DDM	4,4'- diaminodiphenylmethane
DGEBA	Diglycidyl ether of bisphenol A
DMP	2,6-dimethyl phenol
DSC	Differential scanning calorimetric
EP	Epoxy porous
EP-CB	Epoxy porous filled carbon black
EP-SD	Epoxy porous filled sodium bicarbonate

ESO	Epoxy soybean oil
OBSH	Oxybisenzenesulphonylhydrazide
OGPA	Open-graded porous asphalt
O/W	Oil-in-water
PPO-EP MS	Poly(phenylene oxide)-epoxy polymer microspheres
SEM	Scanning electron microscopy
T140	Conductive epoxy porous produce by emulsion temperature at 140 °C
T160	Conductive epoxy porous produce by emulsion temperature at 160 °C
T180	Conductive epoxy porous produce by emulsion temperature at 180 °C
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TOFAS	Tall oil fatty acids
W/O	Water-in-oil

LIST OF SYMBOLS

Ω	Ohm
CO_2	Carbon dioxide
eq	Equivalent
MPa	Mega Pascal
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
Pa	Pascal
pH	Potential Hydrogen
phr	Parts per hundred
ppm	Parts per million
rpm	Rotation per minute
S/m	Siemens / Meter
V	Voltage
wt%	Weight percentage

LIST OF EQUATIONS

Natrium Bikarbonat sebagai Ejen Peniupan keatas Morfologi dan Sifat-sifat Bagi Konduksi Epoksi Berliang Terisi Karbon Hitam yang Disediakan daripada Sistem Pengemulsi

ABSTRAK

Kajian ini melaporkan satu kaedah emulsi tunggal untuk menghasilkan konduksi epoksi berliang (CEP), yang bertindak sebagai bahan tambah pengalir elektrik. CEP adalah direka untuk mengatasi kandungan tinggi menggunakan pengisi pengalir dalam komposit dan menyediakan penyerakan pengisi yang lebih baik. Konduksi epoksi berliang (CEP) telah direka dari campuran epoksi, pengeras poliamida, pengisi hitam karbon dan natrium bikarbonat. Pengisi hitam karbon bertindak sebagai pengalir bahan tambah manakala natrium bikarbonat bertindak sebagai ejen peniupan. Natrium bikarbonat dipilih kerana kos dan pembentukan gas yang tidak bertoksik. Campuran epoksi dititiskan ke dalam minyak jagung yang dipanaskan dengan suhu yang berbeza. Oleh kerana ketidakbolehcampuran epoksi dengan minyak jagung, titisan epoksi telah dihasilkan. Titisan epoksi yang pertama telah dipecahkan kepada titisan-titisan kecil kerana dikenakan rincihan semasa pengacauan. Tambahan lagi, gas terurai (gas karbonik dan wap air) daripada natrium bikarbonat juga disebabkan tekanan berkembang dalaman yang selanjutnya memecahkan titisan epoksi ke titisan halus yang banyak. Tindakbalas pematangan epoksi dan poliamida berlaku serentak untuk membentuk CEP. Disebabkan ini, hitam karbon telah diserakkan ke seluruh liang. Hasil kajian ini menunjukkan bahawa pengemulsi pada suhu 160 °C mempamerkan sebagai suhu optima untuk menghasilkan kumpulan yang besar zarah berliang epoksi. Selain itu, kesan daripada kandungan hitam karbon keatas morfologi, sifat-sifat haba dan sifat-sifat konduksi epoksi berliang telah dikaji. Kajian ini didapati bahawa saiz zarah CEP menjadi lebih kecil dengan peningkatan kandungan hitam karbon. Penggunaan 20 bsr kandungan hitam karbon merupakan kandungan optima mempamerkan pengaliran elektrik tertinggi dengan penambahan 20 wt% CEP ke dalam epoksi-polyamina sebagai agen pematangan. Kebaikan menggunakan CEP versus komposit epoksi-poliamina yang diisi dengan karbon hitam secara langsung dibuktikan dari peniningkat yang lebih tinggi. Seperti yang dijangkakan, kandungan natrium bikarbonat yang tertinggi (20 bsr dalam CEP menggalakkan pengaliran elektrik yang lebih baik iaitu 3.7409×10^{-6} S/m.

Sodium Bicarbonate as Blowing Agent on Morphology and Properties of Conductive Carbon Black-Filled Epoxy Porous Prepared by Emulsion System

ABSTRACT

This study reported a single emulsion method to produce conductive epoxy porous (CEP), which worked as a conductive additive. The CEP was fabricated to overcome the high content of conductive filler using in composite and provide better filler dispersion. Conductive epoxy porous (CEP) had been fabricated from the mixture of epoxy, polyamide hardener, carbon black filler and sodium bicarbonate. Carbon black filler worked as conductive additive while sodium bicarbonate worked as blowing agent. Sodium bicarbonate was selected because of cost effectiveness and non-toxic gases formation. Epoxy mixture was dropped into a heated corn oil with different temperature. Because of the immiscibility of epoxy and corn oil, epoxy droplets were formed. Initial epoxy droplets were broken into smaller droplets due to the applied stirring shear. In addition, the decomposed gas (carbonic gas and water vapour) from sodium bicarbonate also caused an internal expanding pressure to further break the epoxy droplet into many fine droplets. Curing reaction of epoxy and polyamide occurred simultaneously and formed CEPs. Through this, carbon black was dispersed throughout the porous. The results showed that emulsion temperature at 160 °C was selected as the optimum temperature to provide the large packing group of epoxy porous particles. On the other hand, the effect of carbon black content on morphology, thermal properties and electrical properties of conductive epoxy porous was studied. It was found that epoxy particle in CEP became smaller with the high carbon black content. The use 20 phr carbon black content was optimum content exhibited highest electrical conduction by adding of 20 wt% CEP into epoxy-polyamine as binder. The advantageous of CEP versus direct carbon black filled epoxy-polyamine composite is proven form the higher conducting. As expected, the highest sodium bicarbonate content (20 phr in CEP) exhibited promoted better electrical conductivity which is 3.7409×10^{-6} S/m.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, applications of conductive polymer composites (CPC) in electronic packaging are widely commercialized thanks to their advantages over metals, such as corrosion resistance, low density and inexpensive (Teh et al., 2011). Commonly, CPC is prepared by adding conductive filler into polymer matrix (especially epoxy resin). Conductive filler plays a role of electrical conduction, while polymer matrix helps to shape CPC into product design (Chung, 2001). The shaping process of CPC is easier and cheaper compared to metal. The common conductive fillers used are carbon sources (carbon black, graphite and carbon nanotube) and metal particles. Normally, high filler loading is required to achieve the desired conductivity, which could raise the cost issue. Furthermore, another common drawback is the sediment of conductive filler in CPC due to the high density of conductive filler compared to that of polymer matrix. To overcome these drawbacks, conductive microspheres have been introduced, which are the conductive filler-coating microsphere.

Conductive microspheres have been paid excessive attention by researchers and industries (Wei et al., 2012; Xuemei & Hao, 2013; Jain et al., 2013). The development of conductive microspheres continuously improves to meet desired applications. Conductive microspheres can be obtained by coating conductive filler on the surface of non-conductive microspheres. The common microspheres used widely are glass microspheres, cenospheres, carbon microspheres and polymer microspheres. Conductive microspheres have many advantageous properties such as similar density to polymer matrix, high specific surface area, excellent thermal property and reasonable electrical conductive property. Hence, conductive microspheres have been used to replace bare conductive filler in CPC and applied in electronic, biomedical and sensor devices (Qian et al., 2007). Tao et al. (2015) fabricated conductive microspheres for flip-chip interconnection. They discovered that the using of conductive microspheres offer the better alternative way to attain fine pitch interconnection and reducing material cost due to reduced particle usage.

Previous study on conductive polymer composite (CPC) showed a higher loading of conductive filler required to accomplish excellent electrical properties. Suherman et al. (2015) studied the electrical conductivity of graphite/epoxy composites. They found that the electrical conductivity of natural graphite/epoxy composites was 11.5 S/m at 75 wt% whereas the electrical conductivity of synthetic graphite/epoxy composites was 6.35 S/m at 75 wt%. The usage of higher loading of conductive filler caused increase in cost and also affect to properties of final product (Planes et al., 2012). Furthermore, the use of metal as conductive filler in conventional composite has been studied. The electrical conductivity of epoxy/metal (Al, Zn, Sn) increases with increasing filler volume fraction (Boumedienne et al., 2017). The high weight density of metal results the phase separation during curing. The poor filler dispersion induces to a bi-layer formation in a conventional composite. To overcome these problems, the invention and production of metal coated cenospheres as conductive microspheres are widely studied and used in much electronic applications.

The metal coated cenospheres is considered as one of the most advanced conductive materials to reduce the conductive filler used in conductive composites. However, there are some limitions in applications of these conductive cenospheres as well as the difficulties encountering during process. The usage of metal coated cenospheres have to be caredon the wetability of metal surface with the matrix binder. In addition, the metal coating process onto the cenospheres commonly used is electroless plating (Aixiang et al.,2005). Electroless plating method is complicated method which conducted using two-step process of surface sensitizing and metal plating (Tae & Sung, 2014). The main factor of electroless plating method that need to be considered during fabrication metal coated cenospheres is their surface tension and wettability between two surfaces (Duncan et al., 2006). In addition, the cost production is also need to be considered. Therefore, the idea of conductive porous is introduced which could promise more advantageous on filler-polymer matrix adhesion and better filler dispersion.

Conductive porous is actually also fabricated from polymer composite. The most suitable polymer to produce conductive porous is epoxy. It is because epoxy is the most popular thermoset polymer widely used in electronics. Hence, conductive epoxy porous and epoxy matrix could provide a better adhesion and well mechanical properties and conduction. In addition, the porosity of porous materials could affect electrical behavior of the porous materials. The electrical behavior of the porous composites decreases with the increase in porosity (Wang et al., 2013). Epoxy has excellent mechanical properties, excellent thermal properties better chemical resistance because of its three-dimensional crosslink via the curing reaction between epoxy and hardeners (Li et al., 2016; Zhou et al., 2013). The epoxy resin and hardener ratio also called as stoichiometric, which plays important role in determining the properties of cured resin (Bignotti et al., 2011). In addition, ratio of epoxy and hardener can be varied to excess of epoxy or hardener to produce adducts system. Polyamide-epoxy adduct, which reversed ratio of epoxy and polyamide ratio using excess stoichiometric polyamide content, is reported to use for fabrication of epoxy micro-balloon and epoxy foam. This adduct system exhibited a flexible three dimension crosslink polymer because of low polymer chain between crosslink and low crosslink density (Fauzi et al., 2015).

Single emulsion can be considered as the most suitable technique to produce conductive microspheres due to the advantageous such as simple and economic process. Bakar et al. (2009) produced epoxy micro-balloons by single emulsion method. The epoxy mixture was dropped and stirred in heated silicone oil. Due to immiscible between epoxy mixture and silicone oil, the epoxy mixture droplets form a spheres shape in heated silicone oil. These epoxy mixture droplets contain blowing agent, thus, this epoxy droplets blown and simultaneously cured after receiving heat from silicone oil. The foaming process could be improved by using blowing agent. Selection of blowing agents is essential because it will affect the properties of polymer. The common blowing agents usually used are sodium bicarbonate because of low cost and green. Therefore, the addition of conductive filler into epoxy mixture could introduce a conductive epoxy porous. The production of conductive epoxy porous helps mostly in an economical way as they reduce the filler content usage in conductive composite.

Besides, they are easy to disperse on the epoxy matrix as it has lower density. Hence, there are no phase separation will be occurred in composite. In addition, conductive epoxy porous could have the closed surface tension to the matrices, hence provide a good wettability and well adhesion to the matrix. The carbon black is expected to disperse on the porous's wall in advance. The dispersion of carbon black on the porous's wall is to provide conductive properties to the porous. Additionally, the cost for carbon black is cheaper than metal. The production of conductive epoxy porous is a one step process compared to metal-coated cenosphere, as a result, a lot of time saving and low cost are advantageous. Further practise to reduce cost is appliance green materials and cheap such as sodium bicarbonate as blowing agent.

Blowing agents are substances that can introduce a cellular structure through foaming process to polymer matrix. Blowing agent will liberate gases in polymer matrix once decomposition temperature obtained. The selection of blowing agent based on its decomposition temperature, its decomposition gas and cost are important. Sodium bicarbonate which used in this study, is an inorganic chemical blowing agent in which seldom used due to their attractive advantages such low cost and non-toxic of all decomposed product (Muralisrinivasan, 2013). It will produce sodium carbonate salt, gas of carbon dioxide (CO_2) and water (H_2O) vapour during decomposition process once decomposition temperature achieve (Bakirtzis et al., 2009).

1.2 Problem Statements

Epoxy is one of the most common polymers used to produce conductive materials. The common epoxy composite is prepared by using casting the mixture of epoxy, which composes of conductive filler and hardener. The new explore in electronic materials is focusing on cost reducing by minimizing the content of conductive filler and simplifying the production processing. Previous study on conductive polymer composite (CPC) displayed a higher loading of conductive filler required to accomplish excellent electrical properties. The usage of higher loading of conductive filler caused increase in cost and also more cautions on filler's dispersion and sedimentation (Planes et al., 2012). To overcome these problems, the invention and production of conductive epoxy porous is investigated, which is considered as pre-dispersing filler porous so that a better electrical conductivity could be achieved with low filler content. This production method is one process compared to two processes of conductive filler coated cenospheres (fabrication process of cenosphere and coating process).

In previous study, the epoxy micro-balloon was fabricated by single emulsion system was done. Due to a mixture of immiscibility two liquids between epoxy mixture and oil, the small droplets of one liquid are formed and being dispersed throughout the other. The advantageous of manufacturing process is simple and low cost (Bakar et al., 2009). The used of reversed ratios of epoxy and polyamide as called polyamide-epoxy adduct in which the excess polyamide used to produce longer chain and higher molecular weight compared to epoxy. Longer chain from the polyamide promotes induces lower crosslink density induces a low crosslink density of the cured matrix. It resulted in a flexible and expandable epoxy was obtained (Fauzi et al., 2015).

The epoxy micro-balloon was produced without using conductive filler so the system was simpler compared to the epoxy system with conductive filler because of