UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERISATION OF Y3Fe5O12-FILLED POLYVINYLIDENE FLUORIDE COMPOSITE

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By

MOHD HASHIM MOHD SAAD

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Buat isteri tersayang, Nurul Anisyah, anak-anakku Najmi and Humaira… Abah dan Mak… inilah hasil dari pengorbanan semua.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : Associate Professor Noorhana binti Yahya, PhD

Faculty : Science

This research project was undertaken with the main objective of preparing and characterising a wave absorbing material by utilising a magnetic material with polymer as the base material to provide the carrier template. Polyvinylidene fluoride (PVDF) was chosen as the polymer due to the well-established physical properties. Yttrium iron garnet (YIG) was chosen as the magnetic filler due to its well known microwave absorbing properties.

Preparation of YIG particles was carried out via a sol-gel method from nitrates raw material with a citrate route. It was found that with this method employed, the sintering temperature of YIG was minimised to 800ºC compared to 1300ºC for a normal solid state reaction method. PVDF powder was supplied by manufacturer and its film was prepared by dissolving it in cyclopentanone. This method was chosen to reduce the heating cost of preparation as a normal preparation would require hot melting of the

PVDF powder. It was found that up to 30 weight percent (wt%) of PVDF could be dissolved in cyclopentanone successfully. Higher wt% hindered total dissolution of PVDF. Dissolution of PVDF powder in cyclopentanone was carried out by magnetic stirring at about 200 RPM for half an hour followed by another half an hour of stirring and heating (200 RPM and 90ºC). The whole process was carried out under reflux condition and the gel formed after the stirring was left to cool down for a few minutes. The gel was cast onto a petri dish to form film. PVDF-YIG composite was prepared by the same PVDF preparation method with additional YIG particles prepared as a raw material component. The composition of YIG is limited to 20 wt%.

It was found that YIG particles prepared had an average crystallite size of about 51 nm and YIG single phase was formed at sintering temperature as low as 600ºC. Temperature of 800ºC was chosen as the sintering temperature for preparation of YIG filler particles for the composite due to a better garnet phase formed as observed by XRD. PVDF with 10 wt% of PVDF dissolved in cyclopentanone was chosen for the composite preparation. The PVDF film prepared was found to be highly crystalline with a major XRD peak observed at 77.7º (2θ). This peak was never reported before for PVDF. The PVDF film had leaf-like morphology with observable fibrils. FT-IR results confirmed the YIG and PVDF prepared conformed to reported results. EDX analysis showed that all elements were traceable although with some deviation from theoretical values.

Magnetic analysis of YIG, PVDF and PVDF-YIG composites showed that all the samples prepared were wave absorbing. It was found that the PVDF film without any filler was a magnetic material and had a better wave absorbing property than the YIG itself. It was also found that imaginary permeability of composite samples showed a capacitive instead of inductive character. However, the best wave absorber was found to be the composite with 1 wt% of YIG filled which can operate at a frequency range of 2 MHz – 1 GHz with a real permeability of about 200.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN UNTUK KOMPOSIT POLIVINILIDENA FLORIDA TERISI-$Y_3Fe_5O_{12}$

Oleh

MOHD HASHIM MOHD SAAD

Ogos 2007

Pengerusi : Profesor Madya Noorhana binti Yahya, PhD

Fakulti : Sains

Projek penyelidikan ini telah dijalankan dengan tujuan utama untuk menyediakan dan mencirikan bahan penyerap gelombang dengan menggunakan bahan magnet dan polimer sebagai bahan asas yang memberikan templat pembawanya. Polivinilidena florida (PVDF) telah dipilih sebagai polimer tersebut kerana sifat-sifat fiziknya yang telah diketahui secara meluas. Garnet besi itrium (GBI) pula dipilih sebagai bahan magnet pengisi kerana sifat penyerapan gelombang mikronya yang terkenal.

Penyediaan partikel-partikel GBI telah dijalankan melalui kaedah sol-gel dari bahan mentah nitrat dengan laluan sitrat. Dengan kaedah yang digunakan, didapati suhu rawatan haba bagi pembentukan struktur garnet GBI telah dapat diturunkan ke 800ºC dari 1300ºC yang biasa digunakan untuk kaedah keadaan pepejal. Serbuk PVDF telah diperolehi dari pengeluar dan filemnya telah disediakan dengan melarutkannya di dalam siklopentanon. Kaedah ini telah dipilih untuk mengurangkan kos pemanasan bagi

penyediaan kerana biasanya, penyediaan filem PVDF adalah dengan pencairan haba serbuk PVDF. Didapati, PVDF dapat dilarutkan dengan sempurna sehingga 30 peratus berat dalam siklopentanon. Peratus berat yang lebih tinggi didapati menghalang pelarutan sempurna PVDF. Pelarutan serbuk PVDF di dalam siklopentanon telah dilakukan dengan mengacau menggunakan pengacau magnet pada kelajuan kira-kira 200 pusingan seminit selama setengah jam diikuti pengacauan dan pemanasan selama setengah jam pada kadar 200 pusingan seminit dan 90ºC. Keseluruhan proses dijalankan di bawah keadaan refluk dan gel yang terhasil selepas pengacauan dibiarkan sejuk selama beberapa minit. Gel kemudian dituangkan ke dalam piring petri untuk mebentuk filem. Komposit PVDF-GBI telah disediakan dengan kaedah penyediaan yang sama dengan tambahan partikel-partikel GBI sebagai bahan mentah tambahan. Peratus berat GBI telah dihadkan setakat 20 peratus berat PVDF.

Partikel-partikel GBI yang disediakan didapati mempunyai saiz hablur 51 nm dengan fasa tunggal GBI dapat dilihat pada suhu rawatan haba serendah 600ºC. Bagaimanapun, 800ºC dipilih sebagai suhu rawatan haba untuk penyediaan partikel-partikel yang seterusnya untuk penyediaan komposit kerana fasa garnet yang lebih baik dapat dilihat pada puncak XRD pada suhu ini. PVDF dengan 10 peratus berat PVDF dalam siklopentanon telah dipilih untuk penyediaan komposit. Filem PVDF yang disediakan didapati bersifat hablur dengan puncak XRD utama pada 77.7º 2θ. Puncak ini tidak pernah dilaporkan sebelum ini. Filem PVDF didapati mempunyai morfologi seperti daun dengan fibril-fibril turut kelihatan. Keputusan FT-IR mengesahkan GBI dan PVDF yang disediakan menepati keputusan yang pernah dilaporkan sebelum ini. Analisis EDX

menunjukkan semua unsur-unsur dapat disurih walaupun terdapat sedikit penyisihan dari nilai teori.

Analisis magnet bagi GBI, PVDF dan komposit PVDF-GBI menunjukkan semua sampel menyerap gelombang. Didapati filem PVDF tanpa sebarang bahan pengisi merupakan bahan magnet dan mempunyai sifat penyerapan gelombang yang lebih baik dari GBI sendiri. Didapati juga, ketelapan khayalan sampel-sampel komposit adalah bersifat berkapasitans, bukannya aruhan. Bagaimanapun, penyerap gelombang yang terbaik dari sampel-sampel ini ialah komposit dengan 1 peratus berat BIG terisi yang dapat beoperasi pada julat frekuensi 2 MHz sehingga 1 GHz dengan ketelapan sebenar kira-kira 200 sepanjang julat tersebut.

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In the name of Allah, Most Gracious and Most Merciful. All thanks and praise is to Allah for without His grant, this thesis can never be completed.

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Last but not least, all my family, without all these sufferings, this can never be realised.

I certify that an Examination Committee has met on 21st August 2007 to conduct the final examination of Mohd Hashim bin Mohd Saad on his Master of Science thesis entitled "Preparation and Characterisation of $Y_3Fe_5O_{12}$-Filled Polyvinylidene Fluoride Composite" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the degree of Master of Science.

Members of the Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirements for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 13 December 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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MOHD HASHIM MOHD SAAD

Date: 19 November 2007

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LIST OF ABBREVIATIONS

d_{hkl}	lattice spacing
EDX	Energy dispersive X-ray
FT-IR	Fourier-transform infrared spectroscopy
GHz	Giga hertz
MHz	mega hertz
MPa	mega Pascal
PVDF	poly(vinylidene fluoride)
RAM	radar absorbing materials
RPM	round per minute
SEM	Scanning electron microscopy
VPFESEM	variable pressure field emission scanning electron microscopy
wt%	weight percent
XRD	X-ray diffraction
YIG	Yttrium iron garnet ($Y_3Fe_5O_{12}$)

CHAPTER 1

INTRODUCTION

1.1 General

Interest in materials that absorb radio frequency energy has existed for many years. In the digital age all the radio frequency spectrum is utilized, from the quasi-microwave band (1-3 GHz) for wireless telecommunications and electronic measuring equipment, and in radar design up to the millimetre waves in the 70–100 GHz range. Computers generate harmonic noise in the same range. The problem of the interference between various sources, environmental concerns for shielding from electromagnetic radiation, prevention of reflections and multiple reflections, and numerous other applications require efficient, inexpensive, lightweight absorbers of electromagnetic radiation. The shield from electromagnetic radiation can be either reflection (as well as multiple reflections) or absorption based (Chung, 2001). For effective shielding via absorption of unwanted waves, thickness of shielding material is important as absorption loss is proportional to the thickness of shield (Yang et. al, 2005). For certain application, appropriate thickness and strength are important in determining the end product. Since radar wave is also an electromagnetic radiation, the look for absorbing material for the said radiation is inevitable, be it for military use or for public use. This work will look into preparation of radar absorbing material.

1.2 Polymer

Polymer is such a widely used material that some of us take it for granted. If we look closely into our environment, polymer is all around us whether we realise it or not. Essentially, what is a polymer? Poly is a prefix from Greek's *polys* which means many while mer comes from Greek's *meros* which means part. The word polymer itself originated from Greek's *polumerēs* which means consisting of many parts. Generally, a polymer is a molecule with extremely high molecular weight constructed from repetitions of small and simple chemical unit (Billmeyer, 1971).

Polymer exists as natural part of our world as well as synthetic materials which mostly originated from hydrocarbon. Polymer is being utilised in broad area of usage due to its broad physical and chemical properties. A major categorisation is thermoplastics and thermosets. Thermoplastic polymers can melt or soften so that they can flow and can be formed from one shape into another. It can also be dissolved if a suitable solvent can be found. In both cases, melting and cooling and dissolution and precipitation of thermoplastics, do not change its chemical composition. Thermosets, on the other hand, are polymers cross-linked into one giant molecule forming three-dimensional network structure. Due to this, they can not be melted or dissolved but only swollen by suitable solvents to form gels. They can be destroyed into compounds of composition and structure different from the starting material (Rogers and Simha, 1994).

This work will look into utilising poly(vinylidene fluoride) (PVDF), a thermoplastic polymer, as base polymer for composite preparation.

1.3 Radar

Radar is a method of detecting distant objects and determining their position, velocity, or other characteristics by analysis of very high frequency radio waves reflected from their surfaces. Its purpose is to provide estimates of certain characteristics of its surroundings of interest to a user. Commonly, radar is used in detecting the presence, position and motion of objects such as aircrafts, ships, or other vehicles within its vicinity. Radar can also provide information about Earth's surface (or that of other astronomical bodies) or about meteorological conditions such as weather. Radar is often used in combinations or with other elements of more complete systems (eg. super computer) for greater range of sensor capability.

Radar operates by transmitting electromagnetic energy into the surroundings and detecting energy reflected by objects. If a narrow beam of this energy is transmitted by the directive antenna, the direction from which reflections comes and hence the bearing of the object may be estimated. The distance to the reflecting object is estimated by measuring the period between the transmission of the radar pulse and reception of the echo. In most radar applications this period will be very short since electromagnetic energy travels with the velocity of light.

Radar waves scatter in a variety of ways depending on the size (wavelength) of the radio wave and the shape of the target. If the wavelength is much shorter than the target's size, the wave will bounce off in a way similar to the way light is reflected by a mirror. If the wavelength is much longer than the size of the target, the target is polarized that can be described by Rayleigh scattering. However, when the two

length scales are comparable, there may be resonances. Early radars used very long wavelengths that were larger than the targets and received a vague signal, whereas some modern systems use shorter wavelengths (a few centimetres or shorter) that can image objects as small as a loaf of bread or even smaller.

Since radar depends on reflection of radio wave for detection process, objects attempting to avoid detection will angle their surfaces in a way to eliminate inside corners and avoid surfaces and edges perpendicular to likely detection directions. This is in a way, to avoid detection by eliminating reflection of transmitted wave, which leads to odd looking stealth ships and aircrafts. These precautions however, do not completely eliminate reflection because of diffraction, especially at longer wavelengths. This then leads to another angle of radar concept that is absorption.

Radar absorbing materials (RAM) are made with compounds having a high loss energy, which enables them to absorb the incident radiation in synchronized frequencies and dissipate it as heat. The manufacture of RAM basically involves the use of compounds capable of generating dielectric and/or magnetic losses when impinged by an electromagnetic wave. Therefore, an excellent RAM should have certain properties such that; it exhibit strong microwave absorption properties over a wide frequency range; it need to be thin and lightweight, especially for aircraft; and it has simple coating-layer structure and spend less working time during the urgent process (Fan et. al., 2006).

Over the years, radar technologies have been improved drastically with the use of high-powered large bandwidth transmitters, thereby the developments of the stealth

technologies for evading radar detection have become more important (Vinoy and Jha, 1996). Radar wave (radio wave) can be absorbed by materials depending on the materials' properties and the wavelength of the transmitted wave. Generally, absorption is employed to reduce or eliminate reflection by means of absorbing the transmitted wave energy and thereby not giving the receiver a return signal. This in short, is like the transmitted wave is allowed to travel forever thereby giving the radar a zero detection result (no object detected). This research is spurred from this idea of eliminating reflection concern of objects by having radar wave absorbing material developed.

1.3 Soft Ferrites

Ferrites may be defined as magnetic materials composed of oxide containing ferric ions as the main constituent. The term is often restricted to materials having cubic crystal structure of mineral spinel, but it is also loosely applied to magnetic oxides in general irrespective of their crystal structure. There are basically two types of ferrites, which is soft ferrite and hard ferrite. This is not a tactile quality but rather a magnetic characteristic. Soft ferrite does not retain significant magnetization where as hard ferrite has rather permanent magnetization. Ferrites are ceramic materials, and like other ceramic material, they are brittle but normally have sufficient strength for normal handling. They are chemically very stable and can last for a very long time. Ferrites crystallize in three different crystal types, namely, spinel, garnet and magnetoplumbite.