UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

GREEN MAGNETITE NANOCOMPOSITE SHEET USING COPRECIPITATION LOADING METHOD AS A WAVE ABSORBER IN RFID APPLICATIONS

Mohd Khairul Shahril Bin Mustaq Ahmad

Master of Science in Manufacturing Engineering

2014

GREEN MAGNETITE NANOCOMPOSITE SHEET USING COPRECIPITATION LOADING METHOD AS A WAVE ABSORBER IN RFID APPLICATIONS

MOHD KHAIRUL SHAHRIL BIN MUSTAQ AHMAD

A thesis submitted
in fulfillment of the requirements for the degree of Master of Science
in Manufacturing Engineering

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2014

DECLARATION

I declare that this thesis entitled "Green Magnetite Nanocomposite Sheet using Coprecipitation Loading Method as a Wave Absorber in RFID Applications" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted to candidature of any other degree.

Signature : ……………………………………………

Name : Mohd Khairul Shahril bin Mustaq Ahmad

Date : 29th of August, 2014

DECLARATION

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

Signature : ………………………………

Name : Dr. Rose Farahiyan Munawar

Date : 29th of August, 2014

DEDICATION

To almighty Allah s.w.t.

To my beloved mother, father and late grandmother

To my supportive supervisor and co-supervisors

To all my friends and family

ABSTRACT

EM wave absorber had been used to solve the RFID interference problem when it is used in near metallic environment. Synthetic polymeric matrix from various cellulosic pulps were used to produce wave absorbers with magnetite as its main reinforcement using two different approaches namely lumen loading method and in-situ coprecipitation method. Since both methods were a successful in terms of green technology and cost reduction, this study focused on enhancing the previous two methods by introducing a new developed method called as coprecipitation loading method. Besides that, the exploration of the compatibility of paddy straw and recycled paper as the magnetic sheet matrix also was done to add the green technology value. Result obtained reveal that paddy straw and recycled paper are very good candidate to be embedded with nano-magnetite particles thus conforming its compatibility to be used as a substrate to produce the wave absorber. All three loading methods have good degree of loading around 18.4% to 34.4%, and VSM data also shows that the magnetic wave absorbers exhibit good superparamagnetic behaviour. The proposed method consume less power to be produced compared to the previous methods thus contributes to green environmental effects. All samples were tested in the HF RFID application near to metallic environment showing great performance in alleviating the interference problem and recover up to 60% of the distance detection by comparing to the commercial wave absorber. By using the loading methods and substrates proposed, this research contributes to the production of Green Magnetite Nanocomposites Sheets using substrate from paddy straw and recycled paper pulp combined with magnetite nanoparticles. Besides that, the introduction of coprecipitation loading method also enables magnetic sheet to be produced using less energy compared to previous methods. Lastly, samples produced indicate that the green magnetic wave absorber do perform its main purpose in the RFID application near metallic environment.

ABSTRAK

Penyerap gelombang EM telah digunakan untuk menyelesaikan masalah gangguan RFID apabila ia digunakan dalam persekitaran berhampiran logam. Penyerap gelombang boleh dihasilkan daripada matriks polimer sintetik dari pelbagai pulpa selulosa dengan magnetit sebagai tetulang utama dengan menggunakan dua pendekatan berbeza iaitu kaedah 'lumen loading' dan kaedah 'in-situ coprecipitation'. Oleh kerana kedua-dua kaedah tersebut berjaya dari segi teknologi hijau dan pengurangan kos, kajian ini memberi tumpuan kepada memperbaiki mutu dua kaedah sebelumnya dengan memperkenalkan satu kaedah baru yang maju yang dipanggil sebagai kaedah 'coprecipitation loading'. Selain itu, penerokaan keserasian jerami padi dan kertas kitar semula sebagai matriks kepada lembaran magnet juga telah dilakukan untuk menambah nilainya terhadap teknologi hijau. Keputusan yang diperolehi menunjukkan bahawa jerami padi dan kertas kitar semula adalah calon yang sangat baik untuk dimendakkan dengan zarah nano magnetit menjunjukkan keserasiannya untuk digunakan sebagai substrat untuk menghasilkan penyerap gelombang. Ketiga-tiga kaedah pemendakan menunjukkan hasil mendakan yang baik 18.4% kepada 34.4%, dan data VSM juga menunjukkan bahawa penyerap gelombang magnet mempamerkan cirri-ciri superparamagnetic yang sangat baik. Untuk menghasilkan penyerap gelombagn tersebut, kaedah yang dicadangkan menggunakan kuasa yang berbanding dengan kaedah terdahulu dengan itu menyumbang kepada kesan alam sekitar yang hijau. Semua sampel telah diuji dalam aplikasi HF RFID berhampiran persekitaran logam dan ia menunjukkan prestasi yang hebat dalam mengurangkan masalah gangguan ini sehingga 60% daripada pengesanan jarak jika dibandingkan dengan penyerap gelombang komersial. Dengan menggunakan kaedah pemuatan dan substrat dicadangkan, kajian ini menyumbang kepada pengeluaran 'Green Magnetite Nanocomposite Sheet' menggunakan substrat daripada jerami padi dan pulpa kertas kitar semula digabungkan dengan nanopartikel magnetit. Selain itu, pengenalan kaedah coprecipitation loading juga membolehkan lembaran magnet dihasilkan menggunakan tenaga yang kurang berbanding dengan kaedah sebelum ini. Akhir sekali, sampel yang dihasilkan menunjukkan bahawa penyerap 'green magnetic sheet' dapat melaksanakan tugasnya dalam aplikasi RFID berdekatan persekitaran logam.

ACKNOWLEDGEMENTS

First and foremost, I would like to take this opportunity to dedicate my most modest and sincerest gratitude to the almighty ALLAH s.w.t.. In His will, He gives his humble servant the opportunity and ability to complete this study. Despite the obstacle faced, His will also allows me to gather all information and make the right analyses to complete this research and thesis.

Next, I would like to make a special acknowledgement to my dearest supervisor, Dr. Rose Farahiyan binti Munawar from the Faculty of Manufacturing Engineering in the department of Engineering Materials and also the co-supervisor for her, this thesis is able to be finished thus making a great contribution in its field.

I also would like to express my deepest gratitude to my lovely mother, Rohani Mardi, my dear father, and my dear late grandmother, Allahyarhamah Zainab Kassim, for their moral support that makes me always in motivated mode to pursue my dream. Without their support, I can never see the end of this study and will never make it until the end.

Special thanks also to all my dear friends, Nursharafina Zainol, Nadiah Hamid, Fariza Fuziana Yacob, Muhd Hafez Mohamed, Fevilia Nurnadia Adria Syaifoel, Mazlin Aida Mahamood, Anisah Abd Latif, Muhammad Kazimi Muhamad for without them, my study days will be dull and lifeless. Special dedication also to Mr. Jeefferie Abd Razak and Mr. Hairulhisham Rosnan for their help and support throughout the whole progress.

Thank you all.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

RFID	-	Radio frequency identification
Ms	-	Magnetic saturation
XRD	-	X-ray diffraction
FESEM	-	Field emission scanning electron microscopy
VSM	-	Vibrating sample magnetometer
EM	-	Electromagnetic
HF	-	High frequency
M	-	Magnetisation
H	-	Magnetic strength
Hc	-	Coercive force
T_C	-	Curie temperature
T_N	-	Neel temperature
T_B	-	Blocking temperature
T_M	-	Morin temperature
EDX	-	Energy dispersive X-ray
NaOH	-	Sodium hydroxide
PEI	-	Polyethylenimine
ε_r	-	Permittivity

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Radio frequency identification (RFID) is an emerging technology that is increasingly being used in supply chain management. It plays an important role in supporting logistics and supply chain processes because of their ability to identify, trace and track information throughout the supply chain (Zhu *et al.*, 2012). Compared to bar code technology, RFID gives alignment freedom to customers in detecting goods. The bar code requires the sensors to be aligned parallel with the label while RFID has advantage using long range of radio wave frequency detection.

RFID does not work well with metallic goods because metal will bounce off radio waves causing reading process to fail. In metals, the interference also will disrupt the RFID signals, making the supply chain management that involves with metal a challenge (Adams, 2005).

The magnetic sheet for RFID is a kind of functional composite materials that can absorb an electromagnetic wave. The decay of the electromagnetic signal in RFID system will be effectively reduced by using magnetic interference resistance sheet. Not only that, system detection will perform more and sensitivity will be enhanced (AIC Magnetics Ltd., 2012).

As telecommunication is moving up to high-frequency ranges, the applications of ferrite oxides in the micro-wave frequency region have drawn a lot of attention (Pardavi-Horvath, 2000 and Harris *et al.*, 2009). Here, ferrites nanoparticles as filler will be embedded in the lumen to produce a thin magnetic composite. Ferrites are promising materials for high-frequency applications due to their high permeability, broad bandwidth, mild conduction, and low cost (Hsu *et al.*, 2010). In addition, magnetic nanoparticles are good candidates for different electromagnetic wave and radiation absorption applications. For example, magnetic nanocomposites can be used to enhance the permeability of an antenna substrate, which helps in miniaturization of antenna without sacrificing its performance (Koskela *et al.*, 2011).

The magnetic sheets comprise of ferromagnetic materials were developed and verified to be suitable for alleviating metal interference problems in RFID systems (Hsu et al., 2010). Magnetic sheet from magnetic composite are widely used as EM wave absorbers due to its ability to suppress EM interference thus enhance communication signals (Shokrollahi and Janghorban, 2007).

Several studies have been done in producing magnetic sheet as a wave absorber. Shu *et al.* (2010) developed the magnetic sheet by directly coating the ferrite on a piece of release paper to form a sheet with the desired thickness. While Oka *et al.* (2007) proposed an electromagnetic wave absorbing control technique involving the coating-type magnetic wood. Until now, the development of magnetic sheet using magnetite composite is still less known to be used as a wave absorber applications through filling the lumen of natural fibers with magnetic particles.

Fiber's lumen loading with particles can be done in two different ways, mechanically or chemically. The mechanical deposition of the magnetic particles inside of the lumen can be achieved by vigorous agitation of the fibers and filler particles (Green *at el.*, 1982). On the other hand, chemical precipitation to produces the magnetic particles in the lumen, this can be achieved through in-situ method (Ricard and Machessault, 1990).

Thus, in this study, an alternative method to fabricate Green Magnetic Nanocomposites Sheet as a wave absorber in RFID applications was conducted using several loading techniques. Here, several types of natural fiber were used as a matrix. As expected, this new simple method leads to the formation of Green Magnetic Nanocomposites

Sheet that can be used to enhance the performance of RFID antenna tag, which helps to solve the metal interference problem.

1.2 Problem Statement

Most of magnetic composite wave absorber produced by previous researcher used pure ceramic material such as magnetite. It was used due to its excellent properties as a ferromagnetic material at normal bulk size and as a superparamagnetic material when its size is manipulated at nano-scale. However, to use this as pure ceramic material have certain boundaries because of its composite sheet are not flexible and also are very expensive.

Besides pure ceramic, synthetic polymer matrix composite mixed with magnetite filler were also produced due to its flexibility, cost efficiency and compatibility to be used as wave absorber. Most of wave absorber is used in a short term while synthetic polymeric material does not decompose easily in a normal environment. Hence, new materials need to be considered in replacing the polymer in order to promote green technology that can decompose easily. Due to this matter, paddy straw and recycled papers were used to replace pure ceramic material and synthetic polymeric composite to produce the Green Magnetic Nanocomposite Sheet.

Next, previous researcher uses two approaches to produce the green magnetic sheet which is lumen loading and in-situ coprecipitation method. These methods were a huge success, but no research had discussed the power consumption needed to produce the magnetic sheets. Due to that, this research introduces a new approach, which is a hybrid from the previous methods, but uses less energy to produce the same magnetic sheet wave absorber with comparable performance and named as coprecipitation loading method.

1.3 Objectives of Study

The aim of this research was to get an insight of the properties of the green substrates as wave absorber and as an introduction of the new enhanced method called as coprecipitation loading technique. The specific objectives of the research were:

i. To develop new synthesis method to produce magnetite sheet called as coprecipitation loading method and compared with lumen loading method and in-situ coprecipitation method.

ii. To compare magnetite nanocomposite sheets using substrate from paddy straw and recycled paper pulp combined with magnetic nanoparticles by lumen loading, in-situ coprecipitation, and coprecipitation loading methods

iii. To study the magnetite nanocomposite sheet wave absorber performance in terms of reading range of the RFID in near metallic environment.

1.4 Scope of Study

The scope of this project focused on two main parts. The first part was on production of the green magnetite sheets. During the production, paddy straw and recycled paper pulp are used to produce the magnetic sheets. Next, these pulp undergwent loading process to deposits magnetic particles into the lumen of the pulp. Three different loading processes are chosen to produce the samples using lumen loading method, in-situ coprecipitation method and coprecipitation loading method. Two of the methods were successfully introduced by previous researcher while the third method, which was coprecipitation loading technique, was the manipulation of the previous two methods. After the green magnetite sheets had been successfully produced, the performance of the magnetic sheets are tested and analysed. Then the green magnetic sheets will be characterised to determine the physical, mechanical and chemical properties using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Vibrating Sample Magnetometer (VSM). Besides that, other technique to characterise the samples also were done using degree of loading method and power consumption calculation.

Next, the second stage was to evaluate the performance of the samples. The evaluation was base on the interference of RFID reading process in near metallic environment application. The testing was done by setting up an environment that suit with the near metallic environment. After the environment was set up, the samples were placed accordingly with the tag and reader and the distance performance was evaluated. In order to explain more in terms of the reading range, permittivity testing was done to study on the dielectric properties of the samples and how the near metallic environment mechanism was solved.

CHAPTER 2

LITERATURE REVIEW

2.1 Chapter Overview

This chapter gives an overview on previous research related to this study. It starts with the problem arise from RFID reading process near metallic environment and its possible solution which is by using wave absorber. Then it continues with some properties of iron oxides especially magnetite since this magnetic particle was used in producing the wave absorber. Then, it followed by magnetic paper production process and its properties for it is important to understand the behavior before producing the samples. Lastly, this chapter also reviews on paddy straw and recycled paper since it was used as a substrate in producing magnetic paper.

2.2 Radio Frequency Identification (RFID)

RFID stands for Radio Frequency Identification, a wireless communication technology that is used to track and identify objects or perhaps people that is tagged with a certain identity (Hunt, 2007). There are many applications and few of them are applications in supply chain crate, pallet tracking and in point-of-sale used by ExxonMobil's Speedpass. Another application is a system used in toll collection system, which can be found at the entrance to bridge, tunnels, and turnpike. Besides that, it is being used as a device in animal tracking, livestock management and to track pets. RFID is also used in immobilizers and vehicle tracking. Exploration of RFID enables it to be used in infant ID and security which is the form of wrist or ankle band.

According to Ahson and Ilyas (2008), RFID was first developed by Faraday in the mid-nineteenth century. Between 1900 and 1940, discoveries and development of RFID was made which Faraday had discovered the mutual induction concept, which is the base development for far field tags. In 2007, Moscatiello (2007) stated that RFID has distinct advantages over the barcode. For example, most applications in RFID tag can be detected ″hands off″ while scanning barcode needs human intervention. Besides that, RFID tags can be placed inside the packaging or even in the product itself while barcodes must be visible on the outside of product packaging. Other benefit is that RFID tags are not affected by environmental and mechanical effect while the readability of barcodes can be impaired by dirt, moisture, abrasion, or packaging contours and also have better and longer reading range as compared to barcodes technology. Next, RFID tagged items can be read even if they are behind other items, while barcode must have ″line of sight″ to read it. Other than that, RFID tags have read or write memory capability which barcodes do not and also more data can be stored in an RFID tag compared to barcodes.

Once the RFID data is acquired, is can easily be managed by legacy software infrastructures implemented for the purpose of supply chain management and barcode inventory control. Besides that, it is even possible to manage RFID data and barcode data on the same platform applications simultaneously (Ahson and Ilyas, 2008).

Since the year 2000, RFID implementation has experienced an annual growth rate of 24%. The rapid growth in the market for RFID will bring its costs down to the point where RFID tags will soon be competitive with printed barcodes. In addition, there are revolutionary new fabrication techniques that further reduce its costs (Ahson and Ilyas, 2008).

2.2.1 RFID Principle

There are many types of RFID that exist, but at the highest level, it can be divided into two classes which are active and passive. The active tag require power source which the tag is connected to a powered infrastructure or use energy stored in an integrated battery. As the technology advanced, a tag’s lifetime is limited by the stored energy, balanced against the number of read operations the device must undergo. An example of an active tag is the transponder attached to an aircraft that can identifies its national origin. Another example of an active RFID is LoJack device attached to a car, which incorporates cellular technology and a GPS to locate the car if stolen (Want, 2006).

Passive RFID is more preferable because it does not require batteries or any maintenance. It possesses an indefinite operational life and it is much smaller in size which can be fit into a practical adhesive label. Common passive tag was build of three parts: an antenna, a semi conductor chip attached to the antenna, and some form of encapsulation (Want, 2006).

Conservation of energy is implemented in passive RFID tag which the tag's antenna captures energy and transfer to the tag's ID. Then, this energy will be used by the tag to give information needed by the reader. The outer layer which is the encapsulation secures the tag's integrity and protects the antenna and chip from environmental conditions or reagents. The common shape of the passive tag has two shape, the first is in a small glass vial such as in Figure 2.1 (a) or a laminar plastic substrate with adhesive on one side to enable easy attachment to goods such as in Figure 2.1 (b) (Want, 2006).

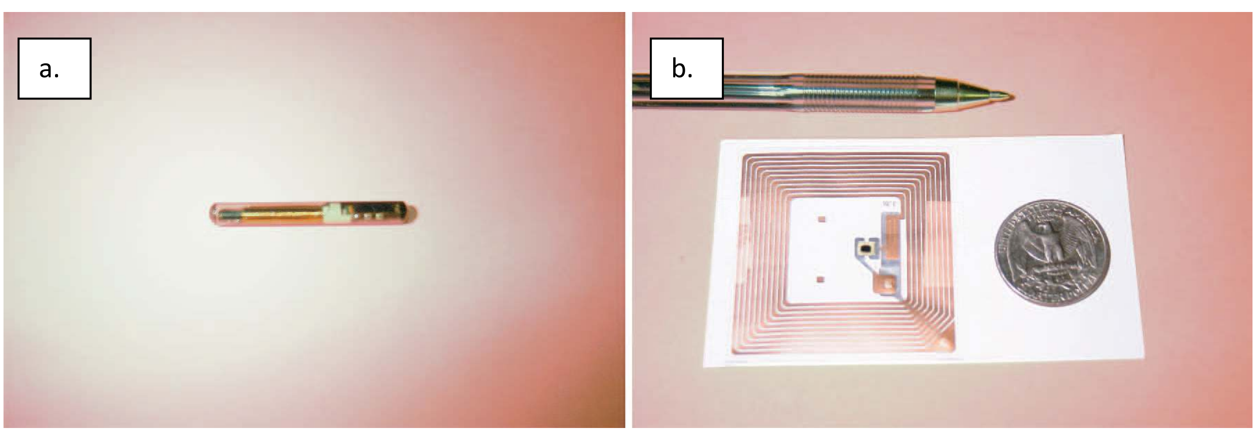

Figure 2.1: RFID tags based on near-field coupling: (a) a 128 kHz Trovan tag, and (b) a 13.56 MHz Tiris tag (Want, 2006).

Want (2006) added that, to date, there are two fundamental designs for powering the tag, which manipulate the magnetic induction and electromagnetic (EM) wave capture. These two designs take advantage of the EM properties associated with an RF antenna which are the near field and the far field. Both can transfer enough power to a remote tag to sustain its operation; typically between 10 μW and 1 mW, depending on the tag type. (For comparison, the nominal power an Intel XScale processor consumes is approximately 500 mW, and an Intel Pentium 4 consumes up to 50 W.) Through various modulation techniques, near and far field based signals can also transmit and receive data.

2.2.2 RFID Problem In Metallic Environment

Metal are widely used because of its properties, reusable, returnable, sturdy, safe, protective, durable and "green". Despite of its good properties, it is hard to manage, if the same type of containers being use for different purposes. This is because, its opacity prevent any viewer to know exactly what is inside of the container. Metal containers and RFID don't mix too well in terms of reading process but can be identified easily using RFID technology with latest mobile asset management solutions (Adams, 2005).

Adams (2005) added that in most phenomena, metal will bounce off radio waves and water will absorb ultra-high frequencies. Besides this, human body will makes a very good shield against RFID signals due to the factor that human body have so much saltwater. In metals, the interference also will disrupt the RFID signals, making the supply chain management that involves with metal, liquid and harsh environment a challenge.

RFID antenna which is attached to metal causes eddy current to generate and absorb RF energy. This eddy current reduces the overall effectiveness of the RFID field. Besides that, it will also create its own magnetic field when it is perpendicular to the metal surface and "cancels" the reader field. This phenomenon is illustrated in Figure 2.2: