Microencapsulation of Commercial Epoxy Resin for Self-healing Coating

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A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering)
Department of Chemical Engineering, Faculty of Engineering
King Mongkut's Institute of Technology Ladkrabang
Academic Year 2016

กระบวนการไมโครเอนแคปซูเลชันของอีพ็อกซีเรซิ่นเพื่อใช้ในสารเคลือบผิวที่สามารถซ่อมแซมตัวเอง

ชยานันต์ แก้วมาลา

ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร
วิศวกรรมศาสตรบัณฑิต สาขาวิชาวิศวกรรมปิโตรเคมี
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
ปีการศึกษา 2559

Title	Microencapsulation of Commercial Epoxy Resin for Self-healing Coating
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Field of Study	Petrochemical Engineering
Advisor	Asst. Prof. Dr. Apinan Namkanisorn

Accepted by the Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

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Abstract

The aim of this project is to develop self-healing coating embedded with epoxy microcapsules. When the surface of the coating is damaged (i.e., scratched), the liquid reactant was released from microcapsules to heal the damage zone. As a result, the coating resumes its ability to protect the substrate. In this project, microencapsulation of a commercial epoxy resin (Core) in a urea-formaldehyde shell was studied. Microcapsules were synthesized by *in-situ* polymerization of monomers in an *oil-in-water* emulsion by varying process parameters (Agitation rate and Core/shell ratio). The effects of these parameters on particle formation, surface morphology, particle size, shell thickness, and particle size distribution of microcapsules were discussed. The chemical structure of microcapsules was characterized by using Fourier Transform Infrared Spectroscopy (FTIR) that confirms microcapsules consist of epoxy resin (Core) and urea-formaldehyde (Shell). Scanning Electron Microscope (SEM) was used to investigate particle formation and surface morphology. Furthermore, the particles size distribution and shell thickness of microcapsules were determined by using Optical Microscope (OM). The SEM and OM results indicate that the agitation rate affects particle formation, surface morphology, particle size, and particle size distribution. The core/shell ratio affects particle formation, surface morphology, and particle size distribution. The shell thickness is independent on the agitation rate and core/shell ratio. The primary result of salt solution immersion test shows that the microcapsules embedded in epoxy coating help improving corrosion resistance on steel pieces.

Keywords: Microencapsulation, *In-situ* Polymerization, Commercial Epoxy Resin, Urea-formaldehyde, Self-healing Coating

เรื่อง	กระบวนการไมโครเอนแคปซูเลชันของอีพ็อกซีเรซิ่นเพื่อใช้ในสารเคลือบผิวที่สามารถซ่อมแซมตัวเอง
โดย	นายชยานันต์ แก้วมาลา
อาจารย์ที่ปรึกษา	ผศ.ดร.อภินันท์ นันมคณิสรณ์
สาขาวิชา	วิศวกรรมปิโตรเคมี
สังกัด	คณะวิศวกรรมศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

บทคัดย่อ

โครงงานนี้มีวัตถุประสงค์เพื่อพัฒนาสารเคลือบผิวที่สามารถซ่อมแซมตัวเองโดยการใส่ไมโครแคปซูลของอีพอกซี่ให้กระจายตัวอยู่ในชั้นของสารเคลือบ เมื่อสารเคลือบเกิดความเสียหาย เช่น การเกิดรอยขีดข่วน จะทำให้ไมโครแคปซูลแตกออก อีพอกซี่ที่อยู่ภายในจะไหลออกมาทำปฏิกิริยากับสารเคลือบและสมานรอยขีดข่วน ทำให้สารเคลือบสามารถปกป้องโลหะได้ดังเดิม โครงงานนี้ศึกษากระบวนการไมโครเอนแคปซูเลชันของอีพ็อกซีเรซิ่น เพื่อสังเคราะห์ไมโครแคปซูลที่มีอีพ็อกซีเรซิ่นเป็นสารซ่อมแซมบรรจุอยู่ภายในแคปซูล (Core) และยูเรียฟอร์มาลดีไฮด์เป็นชั้นห่อหุ้ม (Shell) ด้วยวิธีอินซิทูพอลิเมอร์ไรเซชันของมอนอเมอร์ในสารละลายอิมัลชันชนิดน้ำมันในน้ำ ตัวแปรที่ศึกษาคือ อัตราการปั่นกวน (Agitation Rate) และอัตราส่วนระหว่างสารซ่อมแซมกับชั้นห่อหุ้ม (Core/Shell Ratio) ที่มีผลต่อลักษณะการเกิดอนุภาค ลักษณะพื้นผิวของไมโครแคปซูล ขนาดของอนุภาค ความหนาของชั้นเปลือก และลักษณะการกระจายตัวของอนุภาค การวิเคราะห์หมู่ฟังก์ชันทางเคมีของไมโครแคปซูลด้วยเครื่องฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปคโตรมิเตอร์ (Fourier Transform Infrared Spectroscopy; FTIR) พบว่าไมโครแคปซูลมีองค์ประกอบของอีพ็อกซีเรซิ่นและยูเรียฟอร์มาลดีไฮด์ การวิเคราะห์โดยใช้กล้องจุลทรรศน์แบบส่องกราด (Scanning Electron Microscope; SEM) และกล้องจุลทรรศน์แบบใช้แสง (Optical Microscope; OM) พบว่า ประการที่หนึ่ง อัตราการปั่นกวนมีผลต่อลักษณะการเกิดอนุภาค ลักษณะพื้นผิวของไมโครแคปซูล ขนาดของอนุภาค และลักษณะการกระจายตัวของอนุภาค ประการที่สอง อัตราส่วนระหว่างสารซ่อมแซมกับชั้นห่อหุ้มมีผลต่อลักษณะการเกิดอนุภาค ลักษณะพื้นผิวของไมโครแคปซูล และลักษณะการกระจายตัวของอนุภาค และประการที่สาม ความหนาของชั้นเปลือกนั้นไม่ขึ้นกับตัวแปรทั้งสอง นอกจากนี้สารเคลือบผิวที่มีการกระจายตัวของไมโครแคปซูลยังมีความต้านทานการเกิดสนิมอีกด้วย

คำสำคัญ: กระบวนการไมโครเอนแปซูเลชัน, วิธีอินซิทูพอลิเมอร์ไรเซชัน, อีพ็อกซีเรซิ่น, ยูเรียฟอร์มาลดีไฮด์, สารเคลือบผิวที่สามารถซ่อมแซมตัวเอง

Acknowledgements

This research was partially supported by faculty of teachers and other supporting person. I am impressed for the assistance and would like to thank for all.

I would like to thank Asst. Prof. Dr. Apinan Namkanisorn for his assistance with methodology, experiment procedure and analytical technique. His expert advice greatly improved my working skills in this project.

I would like to thank teachers of the Chemical Engineering Department, King Mongkut's Institute of Technology Ladkrabang for a comment and suggestion in order to improve my work.

I would like to thank the officer at College of Advance Manufacturing Innovation for assistance of a Scanning Electron Microscope.

I would like to thank the officer at the faculty of science, King Mongkut's Institute of Technology Ladkrabang for assistance of an Optical and Inverted Microscope.

Finally, I would like to thank my colleagues for their collaboration, assistance and all of comments.

Chayanan Kaewmala

Table of Contents

Table of Contents (Cont.)

List of Figures

List of Figures (Cont.)

List of Figures (Cont.)

List of Tables

CHAPTER I
INTRODUCTION

1.1 Background

Nowadays, many industrial factories construct process equipment, vessel tank and piping system with metal or steel. They have corrosion problems for many years that become a cause of damage or shorten lifetime. To solve the problems, using paint coating is the most common method to perform [1-3] and self-healing coatings have become an attractive solution for the problem in the last decade [4]. Self-healing coatings have an ability to repair itself when the surface of coatings was cracked. The coatings provide many advantages including corrosion resistance, chemical resistance, mechanical strength and fracture toughness. Not only they increase a lifetime of materials but also decrease a maintenance of equipment, hence reducing of a process cost will be obtained. Self-healing coatings were widely used for protection of corrosion in aircraft structures, vehicles and also structures or equipment in industrial factories e.g. pump, valve, pipe, process vessel, heat exchanger, tank and structural steel.

Self-healing coatings can be classified into two types. First, intrinsic self-healing coatings; polymers have ability to heal themselves without healing agent. They work by intra or inter molecular interaction e.g. Diel-Alder bond, Ru-catalyst shuffling C-C bonds, disulfide link and van der waal's action. Another is extrinsic self-healing coatings; a healing agent is pre-embedded in the coating matrix. Because the extrinsic self-healing coatings have no structural modification of matrix molecules, they are very simple to apply in commercial coatings compare with other approaches. Furthermore, they have grained more attraction in recent years in the role of extrinsic self-healing coatings based on microencapsulation of healing agent [5, 6].

One of techniques that usually uses to synthesize self-healing coating based on microencapsulation of healing agent is a microencapsulation process. This process requires a healing agent to store in microcapsules. If the microcapsules are cracked or scratched, they break and release a healing agent into target areas. Subsequently, they automatically healed by physical and/or chemical interaction. Microencapsulation of healing agent can be classified into five types including (i) Single-capsule system,

(ii) Capsule/disperse catalyst system, (iii) Phase-separated droplet/capsule system, (iv) Double-capsules system and (v) All-in-one microcapsules system. Therefore, to apply the microcapsules in the self-healing coating application, the microencapsulation process is important process for microcapsules synthesis.

Microencapsulation process was a focus of this project. To develop a self-healing coating, an *in-situ* polymerization of microencapsulation technique was used to synthesize epoxy microcapsules. The microcapsules contain an epoxy resin (Core) which was encapsulated in the urea-formaldehyde polymeric shell. First, the microcapsules were prepared by using a healing agent for cores which is an EPOXY RESIN 820 (a commercial epoxy resin). Poly (urea-formaldehyde) was used for a shell of microcapsules. The microencapsulation of epoxy microcapsules were prepared by varying parameters including agitation rate and core/shell ratio. Then, the effects of particle formation, surface morphology, particle size, shell thickness, and particle size distribution were studied. Moreover, a quick test of corrosion resistance was performed on a carbon steel coated coating embedded epoxy microcapsules to access self-healing ability.

1.2 Objective

To develop self-healing coating by microencapsulation of commercial epoxy resin in urea-formaldehyde shell

1.3 Scopes of Work

1.3.1 Synthesize epoxy microcapsules by microencapsulation techniques.

1.3.2 Characterize epoxy microcapsules for chemical structure, particle formation, surface morphology, particle size, shell thickness, and particle size distribution by using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Optical Microscope (OM), and Inverted Microscope (IM).

1.3.3 Characterize the corrosion resistance of a carbon steel coated coating embedded epoxy microcapsules for self-healing ability.

1.4 Methodology

1.4.1 Literature reviews

1.4.2 Select type of shell and core for coating.

1.4.3 Perform experimental work to evaluate the effects of interested parameters such as agitation rate and core/shell ratio.

1.4.4 Characterize physical properties of microcapsules as well as corrosion resistance of coating.

1.4.5 Analyze the experimental results and report writing.

1.5 Expected Outputs

1.5.1 Able to synthesize the epoxy microcapsule using microencapsulation technique.

1.5.2 Improve corrosion resistance of steel surface through self-healing coating.

CHAPTER II
LITERATURE REVIEWS

2.1 Microencapsulation

2.1.1 The Principle of Microencapsulation

Microencapsulation is a process that a liquid core material (healing agent) is encapsulated in a solid polymeric shell which separates or shields the liquid core material form environment. The microcapsules should be pigments or fillers that can be added into the coating and perform their function well such as contain sufficient a number of chemicals with fast reaction, rupture rapidly when damage, good adhesion with a polymer matrix and also remain available while storage, coating and application [5, 7].

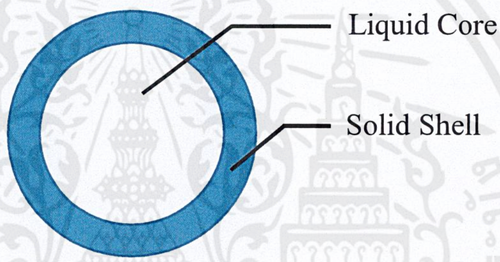


Figure 2.1 A Simplified Illustration of a Microcapsule

Microencapsulation techniques are classified into five types based on a healing agent system, which show in the figure bellow.

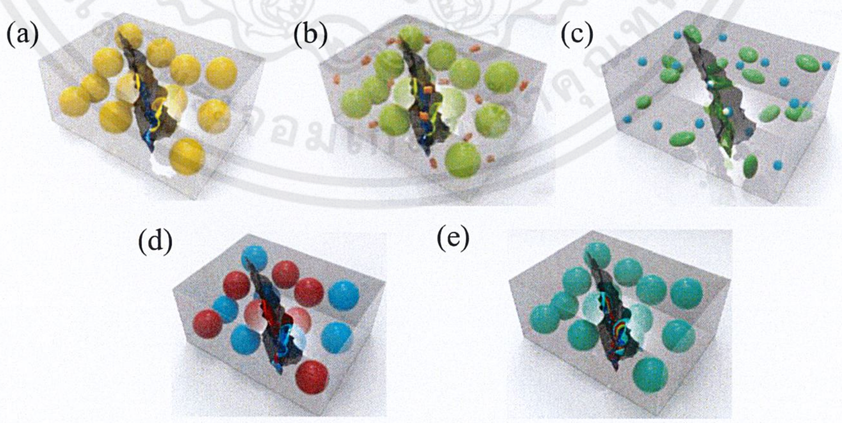


Figure 2.2 The Coating Matrix Embedded Microcapsules of (a) Single-capsule system, (b) Capsule/disperse catalyst system, (c) Phase-separated droplet/capsule system, (d) Double-capsules system, and (e) All-in-one microcapsules system [5]

2.1.2 *In-situ* Polymerization in Microencapsulation

First, oil emulsions in water or water emulsions in oil were produced by agitation. The core material is hydrophobic and acts as disperse phase. The monomers that use for the shell wall are hydrophilic and dissolve in the continuous phase. When the heat was applied and the pH was adjusted, a polymerization started in solution.

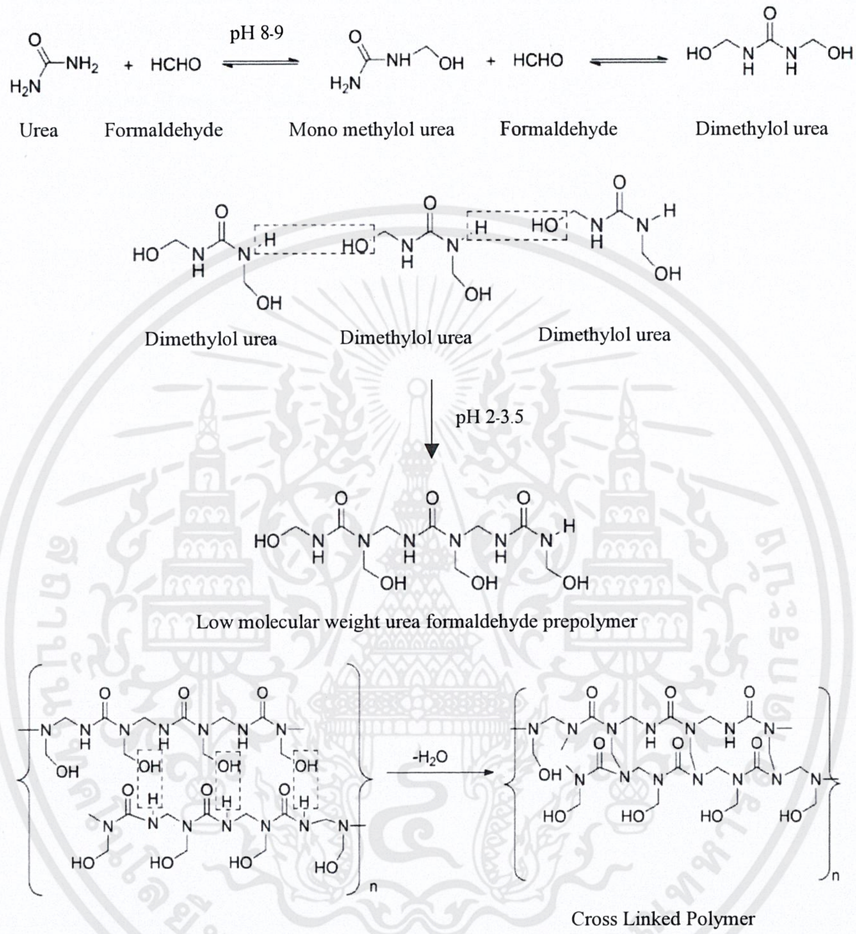


Figure 2.3 A Polymerization of Urea-formaldehyde [8]

An emulsifier which has both hydrophobic and hydrophilic parts acts as a linker to connect the polymeric shell on the surface of the core material droplets. After that, the solution was filtrated and dried. Finally, microcapsules were produced with the desired core material.

There are many advantages of this microencapsulation technique such as controllable microcapsule size and shell thickness, simplicity of procedure, low costs and ease of industrialization. However, compared with other methods, in situ polymerization requires longer reaction times.

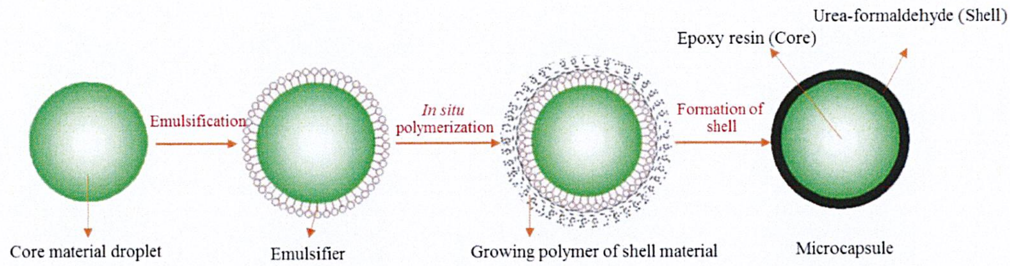


Figure 2.4 A Typical Process of the Microcapsules Formation by *In-situ* Polymerization [5]

2.1.3 Agitation Rate

The purpose of agitation is to form stable emulsion by breaking large epoxy droplets into smaller epoxy droplets. The agglomeration of epoxy droplets is favored at low agitation rate, allowing formation of an unstable emulsion. This affects the polymerization process of the urea formaldehyde shell around the epoxy droplets leading to formation of polymer particles [8].

2.1.4 Epoxy Resin

Epoxies are polymer materials, which begin life as liquid and are converted to the solid polymer by a chemical reaction. An epoxy-based polymer is mechanically strong, chemically resistant to degradation in the solid form and highly adhesive during conversion from liquid to solid. Moreover, its curing can use a wide variety of curing agents at ambient temperatures [9].

2.1.5 Emulsifier

In many literatures [10-12], poly (ethylene-alt-maleic anhydride) (EMA) has been used for an emulsifier to prepare poly (urea-formaldehyde) (PUF) micro-capsules. Different from a small molecular emulsifier such as Sodium Dodecyl Benzene sulfate (SDBS), the macromolecular emulsifier EMA possesses stronger adsorbability and dispensability in oil-in-water emulsion system. It can be explained as follows: when the emulsion is formed, the hydrophilic end of an EMA molecule stretches out its carboxyl group toward the water phase but its hydrophobic end is dissolved in the oil droplet interior. A chain of EMA molecules is very long and has a lot of carboxyl groups on it. With the polymerization, the carboxyl on an EMA molecule will catalyze polymerization and make UF polymer produce around its chain.

The Hydrophilic Lipophilic Balance (HLB) is an indicator of the emulsifying characteristics of an emulsifier. The HLB of an emulsifier is related to its solubility. An emulsifier having a low HLB will tend to be oil-soluble, and one having a high HLB will tend to be water-soluble [13].

Table 2.1 The Relation between HLB Range and their Usage [13]

HLB Range	Usage
4-6	W/O emulsifiers
7-9	Wetting agents
8-18	O/W emulsifiers
13-15	Detergents
10-18	Solubilizers

2.2 Self-healing Coating

Self-healing coating is a coating that has ability to rehabilitate a damage which produced during manufacturing or usage.

2.2.1 Classification of Self-healing Material [14]

Self-healing materials can be divided into two categories; extrinsic and intrinsic, based on the general mechanism of self-healing employed. The difference between these 2 types of self-healing materials are the chemistries.

1) Extrinsic healing systems rely on an external healing agent in the form of capsules or vascular networks. The approaches that often used to prepare are microencapsulation and microvascular network. In both approaches, the self-healing process is initiated by the external/internal damage in the vascular networks as well as the capsules. The capsule shells are typically made of poly (urea-formaldehyde) (PUF); polyurethane; poly (melamine-urea-formaldehyde) (PMUF) and poly (melamine-formaldehyde) (PMF). Different polymerization techniques have been reported to form these capsules. The microencapsulation approach suffers from two major drawbacks including (i) high cost of the catalyst (especially Grubbs catalyst) and (ii) the process of self-healing of materials generally can occur only once since the number of healing-

agents is depleted in the healed region. However, to overcome these limitations, several other approaches have been investigated and are summarized in [14-18].

2) Intrinsic self-healing materials generally are based on either non-covalent chemistries or dynamic covalent chemistries. The non-covalent chemistry approach uses π- π stacking, ligand-metal bonding, and hydrogen bonding. While covalent approaches use Diels-Alder reaction, radical exchange, dynamic urea bond, and trans-esterification. The chemistry of self-healing polymers based on hydrogen bonding, π- π interactions, ionomers, and coordinative bonds has been recently reviewed. The re-formation of chemical bonds in intrinsic materials is triggered by a number of external stimuli including pH change, light, temperature, pressure, or oxygen. Diels-Alder (DA) reactions are most frequently used to create self-healing polymers that utilize reversible bond formation.

Compared with other approaches, self-healing coatings based on micro-encapsulation of healing agents are the most likely to be commercialized in the near future because [19]:

1) To integrate polymers with self-healing abilities, a changing in the molecular structure are not required.

2) Loading healing agent into microcapsules can be easily incorporated into the polymer matrix by using existing blending techniques.

3) Microencapsulation has been developed as a technology since 1950s.

2.2.2 Mechanism of Self-healing Coating Based on Microcapsules

When the surface of the coating embedded microcapsules is damaged (i.e., scratching), the liquid reactant was released from microcapsules to heal the damage zone. As a result, the coating resumes its ability to protect the substrate [19].

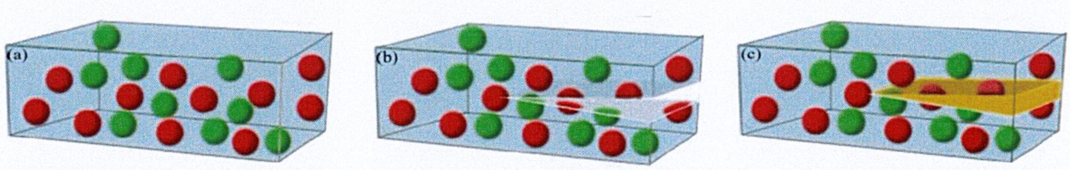


Figure 2.5 Self-healing Process of Microcapsules (a) Original Composites, (b) Crack Propagation, and (c) Self-healing Behavior of Cracking Area [20]

2.2.3 Coating Technique [21]

Doctor blade is one of the widely used techniques for producing thin films on a surface of flat material. The use of aqueous and non-aqueous slurries applied to moving plaster batts by a doctor blade device. When a constant relative movement is established between blade and the substrate, the slurry spreads on the substrate to form a thin film which results in gel layer upon drying

2.3 Healing Efficiency of Self-healing Coating

2.3.1 The Important Factors for Developing Microcapsules

Table 2.2 The Important Factors for Developing Microcapsules [22]

Parameters	Influencing factors
Microcapsule	- Healing agent must be inert to the polymer shell - Longer life of the capsules - Compatibility with the dispersion polymer medium - Weak shell wall to enhance rupture - Proximity to catalyst - Strong interfacial attraction between polymer matrix and capsule shell
Monomer	- Low viscous monomer to flow to the crack upon capillary action - Less volatility to allow sufficient time for polymerization
Polymerization	- Should be fast - Stress relaxation and no cure induced shrinkage - Room temperature polymerization
Catalyst	- Dissolve in monomer - No agglomeration with the polymer matrix
Coating	- Incorporation of microcapsules should have very less influence on physic and mechanical properties of the matrix - Coating thickness must be larger than the microcapsule size - No clustering of catalysts or microcapsules in the matrix polymer and less expensive manufacturing process
Healing	- Should be fast and multiple

2.3.2 Characterization of Microcapsules

Scanning Electron Microscope (SEM) was used to investigate particle formation and surface morphology. The particles size distribution and shell thickness of microcapsules were determined by using Optical Microscope (OM).

2.3.3 Functional Group of Microcapsules [23]

The Fourier transform infrared (FTIR) spectroscopy was used in order to probe the functional group present in epoxy microcapsules

An invaluable tool in organic structure determination and verification involves the class of electromagnetic (EM) radiation with frequencies between 4000 and 400 cm^{-1} (wavenumbers). The category of EM radiation is termed infrared (IR) radiation, and its application to organic chemistry known as IR spectroscopy. Radiation in this region can be utilized in organic structure determination by making use of the fact that it is absorbed by interatomic bonds in organic compounds. Chemical bonds in different environments will absorb varying intensities and at varying frequencies. Thus, IR spectroscopy involves collecting absorption information and analyzing it in the form of a spectrum and the frequencies at which there are absorptions of IR radiation (peaks) can be correlated directly to bonds within the compound.

Because each interatomic bond may vibrate in several different motions (stretching or bending), individual bonds may absorb at more than one IR frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar types of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibrations do not cause absorption of IR radiation. For example, neither of the carbon-carbon bonds in ethene or ethyne absorb IR radiation.

2.4 Corrosion

Corrosion is a process which converts a metal to a more chemically stable form, such as its oxide, hydroxide, or sulfide. It is the destruction of materials or metals by chemical or electrochemical reaction with their environment.

The corrosion can be classified into two types [24]

1) Direct chemical corrosion: the chemical reaction occurs between a surface of metal and gas (e.g. O_2 and SO_2) and then it generates additional metal coat on its surface area e.g. Al_2O_3 coated on Al metal.

2) Electrochemical corrosion: the most of corrosion problem is electrochemical in nature and occurs in an aqueous environment. The aqueous environment is the electrolyte in the corrosion process, through which the electron travels from anode to cathode (i.e., high-potential to low-potential metal). The corrosion process involves the removal of electrons (oxidation) of metal and the consumption of those electrons is termed reduction reactions, often indicated by the presence of oxygen or reduction of water from the aqueous environment, electrolyte etc. [25] The mechanism of rusting of iron are described involves the following steps [26]:

(i) Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidized to ferrous ions.

An anode: $Fe\,(s) \rightarrow Fe^{2+}\,(aq) + 2e^-$

Thus, the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself. These electrons move towards the cathode region through the metal.

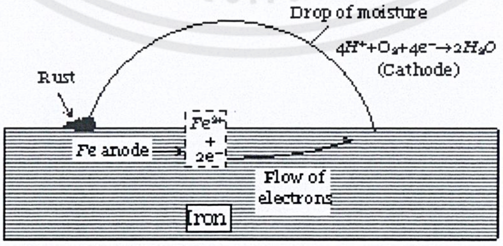


Figure 2.6 Mechanism of Rusting of Iron [26]

(ii) At the cathodes of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The H^+ ions are obtained either from water.

$$H_2O \rightarrow H^+ + OH^-$$

At cathode: $$H^+ + e^- \rightarrow H$$

The hydrogen atoms on the iron surface reduce dissolved oxygen.

$$4H + O_2 \rightarrow 2H_2O$$

Therefore, the overall reaction at cathode of different electrochemical cells may be written as,

$$H^+ + O_2 + 4e^- \rightarrow 2H_2O$$

(iii) The overall redox reaction may be written below

$$2Fe\,(s) + 4H^+ + O_2 \rightarrow 2Fe^{2+}\,(aq) + 2H_2O$$

The ferrous ions are oxidized further by atmospheric oxygen to form rust.

$$4Fe^{2+}\,(aq) + O_2\,(g) + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$$

$$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O \text{ (rust)}$$

2.5 Literature Reviews

Thanawala Karan *et al.* [8] studied about the effect of agitation rate and reaction time in microencapsulation of linseed oil in the poly (urea-formaldehyde) shell for self-healing performance in corrosive environment. The microcapsule mean diameter and shell wall thickness were determined using an optical microscope (OM). The shell thickness increases with increasing reaction time and the particle size is inverted proportional to the agitation rate. The surface morphology of the microcapsules were investigated by scanning electron microscopy (SEM). The rough outer surface morphology provides the additional interfacial area necessary for better adhesion with the film matrix. The chemical structure of microcapsules were characterized by using Fourier transform infrared spectroscopy (FTIR). All the characteristic peaks of UF and linseed oil were found in the FTIR spectra of the microcapsule, which confirms the presence of UF and linseed oil in the microcapsule. Furthermore, they investigated the anti-corrosion ability of the coating embedded with microcapsules, they established the excellent ability of oxidative polymerization of linseed oil released from the ruptured microcapsules in healing the cracks. It prevents further ingress of oxygen and moisture.

Li Yuan *et al.* [10] studied about a self-healing coating with single microcapsule system, which used diglycidyl ether of bisphenol A epoxy as a core material and urea-formaldehyde as a shell material. Preparing microcapsules were done by using differential parameter including (i) Emulsifier stabilizer or surfactant which are Sodium Dodecyl Benzene Sulfonate (SDBS), Octyl Phenol Ethoxylated (OP-10) and Sodium Dodecyl Sulfate (SDS), (ii) Surfactant concentration, (iii) pH value and (iv) Heating rate. Scanning electronic microscope (SEM) and Optimal microscope (OM) were used to observe morphology of microcapsules. They found that (i) The formation of microcapsules is affected by the surfactant type, (ii) The surface and the size of microcapsules can be controlled by the surfactant concentration: increasing the surfactant concentration can reduce the size of microcapsules and enhance the surface roughness of microcapsules, excellent solvent resistance and appropriate mechanical strength and (iii) The adjusting time for pH and the heating rate: no significant influences on the size, core content and yield of microcapsules. The optimal process parameters in this study for synthesizing were using 1wt% of SDBS concentration, 0.2°C·min^{-1} of heating rate and 2-3 hours of adjusting time for pH value.

Qi Li *et al*. [20] studied about a self-healing coating with double-microcapsules, which used diglycidyl ether of bisphenol A epoxy (epoxy resin) and polyetheramine (hardener) for healing agents. Double-microcapsules were prepared by a solvent evaporation technique with the poly (methyl methacrylate) (PMMA) shell. An emulsifier stabilizers were sodium dodecyl sulfate (SDS) and polyvinyl alcohol (PVA), which were used to prepare the epoxy and hardener microcapsules respectively. The double-microcapsules were success by using high-speed agitator at 300-350 rpm. The self-healing composites were prepared by mixing 5, 10, 15 and 10wt% of double-microcapsules in the coating matrix. They investigated the self-healing material by using Scanning electronic microscope (SEM), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA) and Differential scanning calorimetric (DSC). Then found that the 15wt% double-microcapsules with the ratio of epoxy to hardener microcapsules equal to 1.25:1 offered satisfactory repair effectiveness (84.3%) without affecting the mechanical performance of the epoxy composite. The self-healing was carried out successfully at room temperature and high healing efficiency was achieved. Moreover, not only increasing the temperature can increase the self-healing efficiency but its efficiency with double-microcapsules system was higher than the composite with single-microcapsule system due to the easy reaction between the liquid resin and the liquid hardener at the crack surface.

Henghua Jin *et al.* [27] studied about a self-healing coating with double-microcapsules system. One capsule contained a diluted epoxy monomer (EPON 815C) and another capsule contained a modified aliphatic polyamine (EPIKURE 3274). Epoxy microcapsules were prepared by an in situ polymerization method and amine microcapsules were prepared by vacuum infiltration of EPIKURE 3274 into hollow polymeric microcapsules. To perform the microcapsules, the agitator was used in this approach with 800 rpm agitation rate and poly (urea-formaldehyde) was a shell to form pre-polymer on the surface of microcapsules by a poly condensation reaction. Scanning electronic microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA) were used to analysis the self-healing material. After that they found the optimal mass ratio of epoxy: amine capsule was 6:4 and an average healing efficiency is 91% with 10.5wt% of epoxy capsules and 7wt% of amine capsules. But they have some problem in this research, the thermal stability of amine capsule seemly unsatisfied for healing due to the healing efficiency deceased with high temperature cured epoxy.

Simona Cosco *et al.* [28] studied about a self-healing coating with the single microcapsule system. They used a commercial epoxy resin of Bisphenol F (PY306) for a core material and used urea-formaldehyde for a shell of microcapsules. Ethylene maleic anhydride (EMA) copolymer was used as emulsifier stabilizer. So, the urea-formaldehyde microcapsules containing an epoxy resin were prepared by in situ polymerization which varied reaction temperature, reaction time and stirring rate of agitator. To analysis the self-healing material, the scanning electronic microscope (SEM), Differential scanning calorimetric (DSC) and Near-infrared Spectroscopy (NIRS) were obtained. They found that the encapsulation yield as well as the extent of urea formaldehyde polymerization depends on the reaction temperature and the agitation rate, decrease of the reaction temperature as well as of the agitation rate has a great influence on the encapsulation yield.

Chuanjie Fan *et al.* [29] studied about the effect of emulsifier for synthesize microcapsules, which contained poly (urea-formaldehyde) and tetrachloroethylene. The effects of different emulsifiers; including Sodium dodecyl benzene sulfate (SDBS), poly (ethylene-alt-maleic anhydride) (EMA), and Gum Arabic (GA), on morphology and microencapsulation of microcapsules were investigated by Scanning electronic microscope (SEM), Thermogravimetric analysis (TGA) and Optimal microscope (OM). They found that the GA-emulsifier can slow down the deposition rate of resin, which lead to smooth and compact surface of microcapsules. The surface activity of GA was also enhanced by complex formation of GA and SDBS and microcapsules represent good thermal and barrier property.

CHAPTER III
RESEARCH METHODOLOGY

3.1 Chemicals and Equipment

3.1.1 Chemicals

1) EPOXY RESIN 820 (Commercial epoxy resin)
2) Urea
3) Ammonium chloride
4) Resorcinol
5) Deionized water (DI water)
6) Sodium dodecyl sulfate (SDS)
7) 37wt% formaldehyde
8) Hydrochloric acid
9) Sodium Chloride
10) Chloroform

3.1.2 Equipment

1) Magnetic stirrer with hot plate
2) Magnetic bar
3) Vacuum filtration apparatuses
   (Including Vacuum pump, Buchner funnel and side-arm flask)
4) Vacuum oven
5) Breaker
6) Cylinder
7) Volumetric flask
8) Erlenmeyer flask
9) Funnel
10) Separating funnel
11) Stand and clamp
12) Stirring rod
13) Filtrate paper
14) Watch glass

15) Stopwatch

16) Thermometer

17) pH meter

18) Steel plate 25.4x25.4 mm, 1 mm thickness

19) Doctor blade process equipment

20) Finishing sander

3.2 Experimental Procedure

3.2.1 Preparation of Microcapsules Containing Epoxy

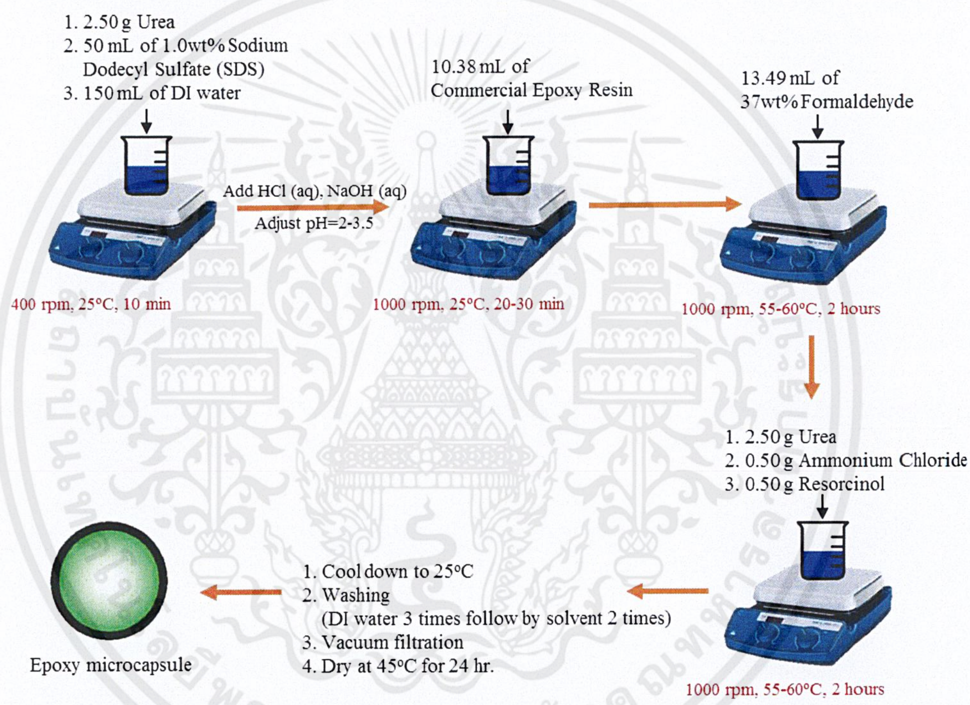


Figure 3.1 Procedures of Epoxy Microcapsules Preparation

1) Add 2.5 g of Urea in 150 mL of DI water in a beaker and stir with 400 rpm of agitation rate of magnetic stirrer for 10 min at 25°C.
2) Add 50 mL of 1.0wt% Sodium Dodecyl Sulfate (SDS) Emulsifier into the solution.
3) Hydrochloric acid (HCl) and sodium hydroxide (NaCl) were used to adjust pH about 2-3.5 and measure pH by using pH meter.

4) Add 10.38* mL of Commercial Epoxy Resin to the solution to form an emulsion. Follow by raising the agitation rate to 1000 rpm.

5) Add 13.49 mL of 37wt% formaldehyde, raise temperature to 55ºC -60ºC. Then, stir at 1000* rpm for 2 hours.

6) After 2 hours, add 2.5 g of Urea, 0.5 g of Ammonium Chloride, and 0.5 g of Resorcinol into the solution. The magnetic stirrer was continuous stirred at 1000 rpm for 2 hours.

7) After finished the reaction, magnetic stirrer and hot plate were switched off and cool down to room temperature (25ºC). During washing this process, use DI water for 3 times and chloroform for 2 times to eliminate the residual epoxy resin which are not encapsulated.

8) The suspension of microcapsules was separated with vacuum filtration at -760 mmHg. Then, use the vacuum oven to eliminate the remaining water at 45ºC for 24 hours.

9) Repeat the step by varying the parameters following Table 3.1.

10) Chemical structure of microcapsules was characterized by using Fourier Transform Infrared Spectroscopy (FTIR). Particles formation and surface morphology were investigated by using Scanning Electron Microscope (SEM).

Note: (*) is varying variables.

Table 3.1 Experimental Variables

Variables	Explanation
Varying variables	• Agitation rate (1000 rpm, 1500 rpm) • Core/shell ratio (3:1, 2:1, 1:1)
Dependent variables	• Particle formation • Surface morphology • Particle sizes • Shell thickness • Particle size distribution
Control variables	• Reaction temperature (55-60ºC) • Reaction time (4 hours) • Emulsifier concentration (1.0wt% SDS)

3.2.2 Preparation of Specimen for Particle Size Analysis

1) Prepare the glass slide and clean the surface.
2) Prepare the coating matrix by mixing of EPOXY RESIN 820 and BONTAMINE 513 with 3:1 of mass ratio.
3) Embed the 10wt% of epoxy microcapsules with the aforesaid coating matrix. Then, stir with 200 rpm of agitation rate at 35°C.
4) Coat the coating embedded with epoxy microcapsules on the surface of glass slide by Doctor Blade Process and control the thickness about 50-150 micrometer.
5) Leave it to dry for 3 days at room temperature (25°C).
6) Analyze the particle size and shell thickness of epoxy microcapsules embed in the coating by Optimal Microscope (OM) and Inverted Microscope (IM).

3.2.3 Preparation of Specimen for a Quick Test of Corrosion Resistance

1) A carbon steel was cut to be 25.4x25.4 mm of area and 1 mm of thickness. Then scrub the surface of steel by a sandpaper.
2) Prepare the coating matrix by mixing of EPOXY RESIN 820 and BONTAMINE 513 with 3:1 of mass ratio.
3) Embed the 15wt% of epoxy microcapsules with the aforesaid coating matrix. Then, stir with 200 rpm of agitation rate at 35°C.
4) Coat the coating embedded with epoxy microcapsules on the surface of a carbon steel by Doctor Blade Process and control the thickness about 50-150 micrometer.
5) Leave it to dry for 3 days at room temperature (25°C).
6) Scratch the dry coating then immerse in the 3.5wt% of NaCl solution for 7 days.
7) Analyze the surface character of self-healing coating.

CHAPTER IV
RESULTS AND DISCUSSION

In this chapter, the chemical structure of microcapsules was characterized by using Fourier Transform Infrared Spectroscopy (FTIR) whereas the particles formation and surface morphology were investigated by using Scanning Electron Microscope (SEM). Subsequently, the particles size and shell thickness of microcapsules were analyzed by using Optical Microscope (OM) and Inverted Microscope (IM), respectively. Furthermore, a corrosion resistance property was roughly observed on the surface of a carbon steel coated with the coating embedded with epoxy microcapsules.

4.1 Chemical Structure Analysis

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the chemical structure of epoxy microcapsules by comparing with epoxy resin and urea-formaldehyde. Typically, the frequencies of infrared radiation are between 4000 and 400 cm^{-1} (wavenumbers).

The Fourier Transform Infrared Spectrum in Figure 4.1 (a) show the IR spectra of commercial epoxy resin. The C-H stretching vibration is observed at the absorption peak between 3000-2800 cm^{-1} that represent -CH group. The absorption peak at 1232 cm^{-1} and 1027 cm^{-1} indicate the presence of C-O stretching (alkyl aryl ether group) of the epoxy resin, respectively.

The Fourier Transform Infrared Spectrum of urea-formaldehyde show in Figure 4.1 (b). The vibration of O-H stretching of hydroxyl group (-OH) is observed on wavenumber between 3500-3200 cm^{-1}. The absorption peak of C-H stretching (-CH_2) is 2951 cm^{-1} The absorption peaks at 1639 cm^{-1} and 1014 cm^{-1} indicate the presence of amide and C-O group, respectively.

The characteristic peaks of both commercial epoxy resin and urea-formaldehyde appear in the FTIR spectra of epoxy microcapsules. The results can predict that the epoxy microcapsules consist of commercial epoxy resin (Core) and urea-formaldehyde (Shell).

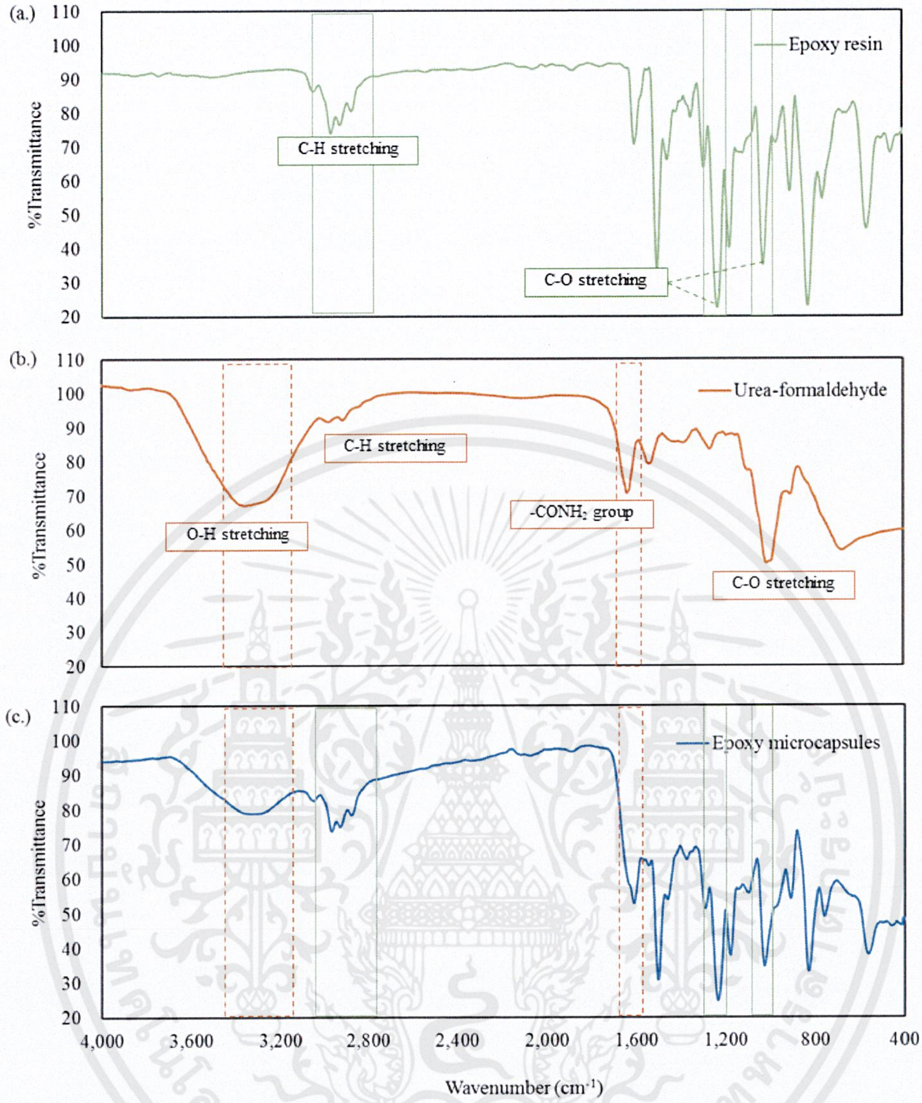
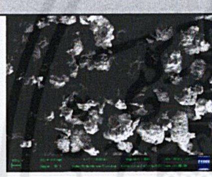
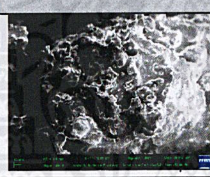
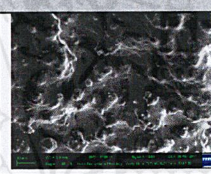
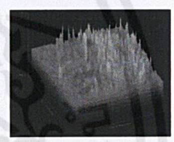
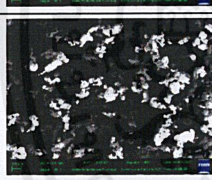
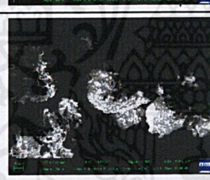
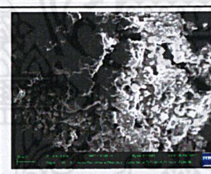
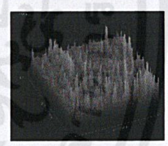
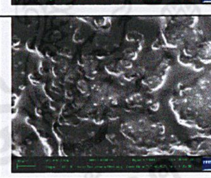
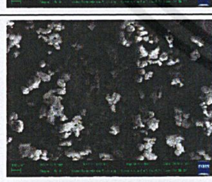
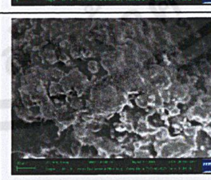
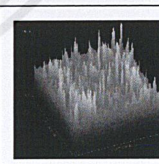
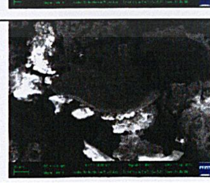
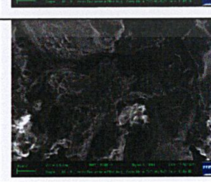
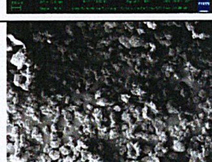
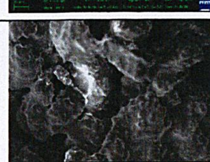
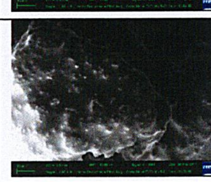


Figure 4.1 Fourier Transform Infrared Spectrum of (a) Epoxy Resin, (b) Urea-formaldehyde, and (c) Epoxy Microcapsules

4.2 Characteristic of Particle Formation and Surface Morphology

The epoxy microcapsules were characterized for particle formation characteristic and surface morphology. In order to characterize surface morphology, ImageJ software were used to perform the surface plot of the SEM images. Then, it can determine the average surface roughness of the epoxy microcapsule. A Root Mean Square (RMS) is a representative of a roughness indicator in this analysis.

Table 4.1 The Particle Formation Characteristic and Surface Morphology of Epoxy Microcapsule in Various Cases

Core/shell ratio	Agitation rate	Magnitude of SEM image			Surface plot (1000x)	Root mean Square (μ^2)
		50x	400x	1000x		
1:1	1000 rpm					71.14
	1500 rpm					77.84
2:1	1000 rpm					75.08
	1500 rpm					98.21
3:1	1000 rpm				N/A	N/A
	1500 rpm				N/A	N/A

4.2.1 Characteristic of Particle Formation

For particles formation characteristic of the epoxy microcapsules was describe in 3 case below.

Case 1: Constant Core/Shell Ratio

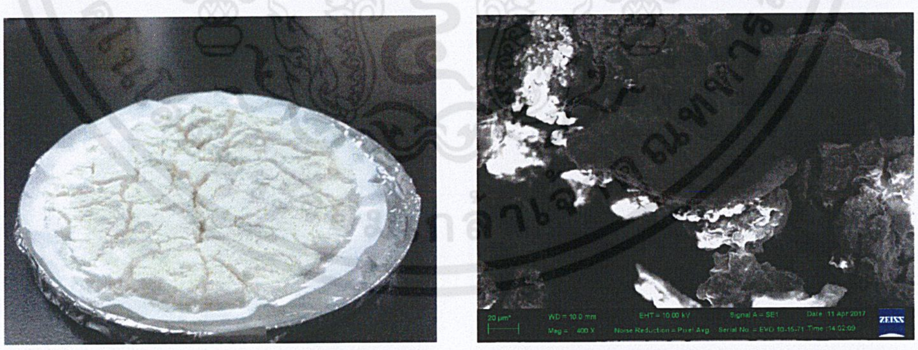
Increasing the agitation rate, the opportunity of microcapsules formation was increased. Resulting in the SEM image of 1:1 and 2:1 core/shell ratio, increasing of agitation rate, the particles are lower accumulate than lower agitation rate. Moreover, resulting more spherical particle shape was observed in higher agitation rate.

Case 2: Constant Agitation Rate

Increasing the core/shell ratio, the opportunity of microcapsules formation was decreased. Increasing amount of core (Epoxy resin) while keeping the amount of shell (urea-formaldehyde) constant results in the weak polymer shell. The polymerization of polymeric shell necessary to have enough urea-formaldehyde to form a polymer around the liquid core.

Case 3: Too High Amount of Core

Resulting in the SEM image of 3:1 core/shell ratio, some of particles were cracked. Because of a high amount of core results poor polymerization of polymeric shell.



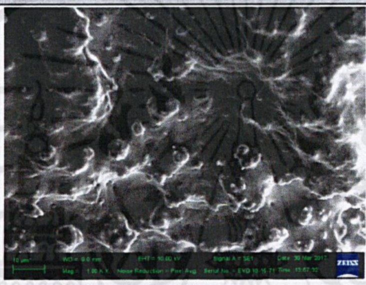
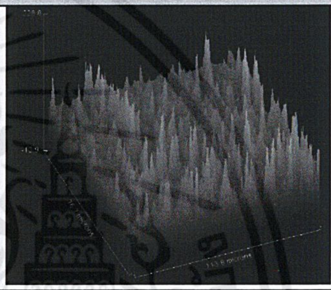
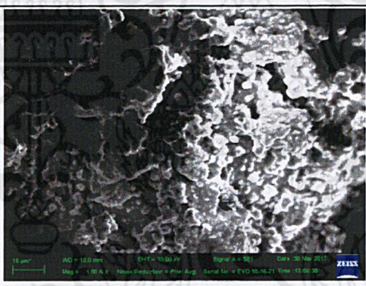
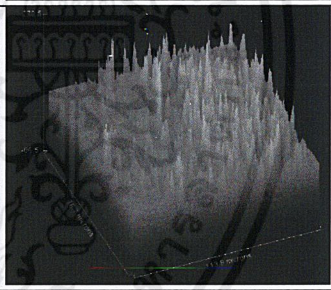
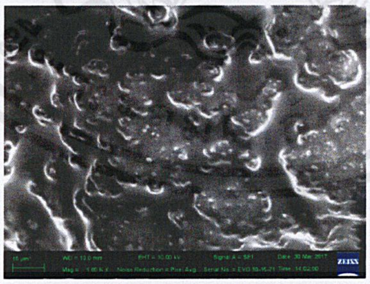
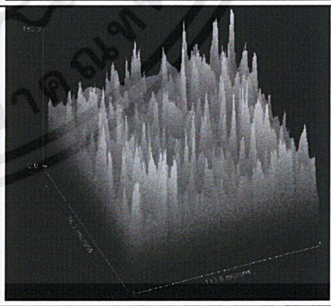
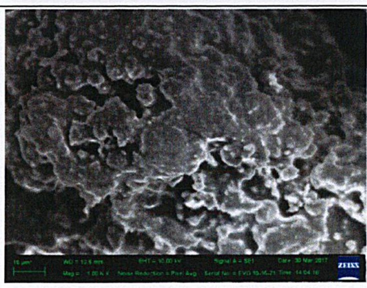
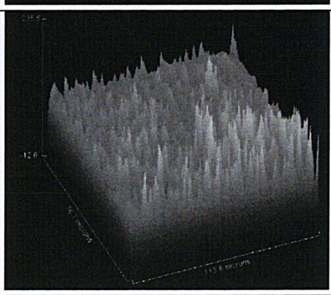
(a) (b)

Figure 4.2 (a) Epoxy Microcapsules Powder after Filtration and Drying, and (b) SEM Image of Cracked Epoxy Microcapsules which Synthesize with 3:1 of Core/shell Ratio and 1000 rpm of Agitaion Rate

4.2.2 Surface Morphology

So, microcapsules which synthesize with 1:1 and 2:1 of core/shell ratio were used to characterize for surface morphology. It is necessary to use the ImageJ software to plot the surface plot as 3D-diagram. Then, determine the average roughness of the epoxy microcapsule surface as a Root Mean Square (RMS) deviation.

Table 4.2 The Surface Morphology of Epoxy Microcapsule in Various Cases

Core/shell ratio	Agitation rate	SEM image (1000x)	Surface plot (1000x)	Root mean square (μ^2)
1:1	1000 rpm			71.14
	1500 rpm			77.84
2:1	1000 rpm			75.08
	1500 rpm			98.21

For the surface morphology of the epoxy microcapsules was described as a roughness characteristic which is dependent on a Root Mean Square (RMS) deviation. It can be describe in 2 case below.

Case 1: Constant Core/Shell Ratio

Increasing the agitation rate, the Root Mean Square deviation was increased. As result, it refers a higher surface roughness which clearly observed at 2:1 core/shell ratio.

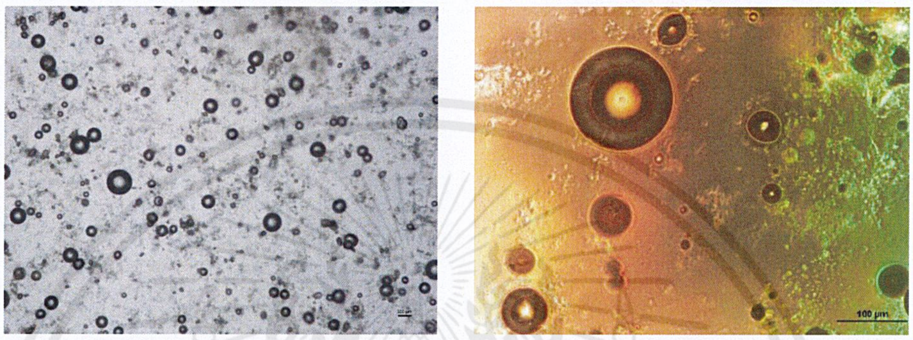
Case 2: Constant Agitation Rate

Increasing the core/shell ratio, the Root Mean Square deviation was increased. As result, it refers a higher surface roughness.

4.3 Particle Size and Shell Thickness Analysis

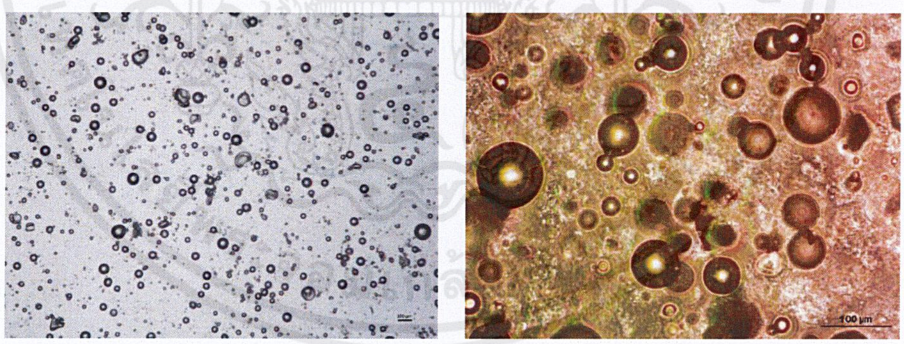
4.3.1 Average Diameter Size and Relative Thickness

First, the epoxy microcapsules were dispersed in the coating matrix condition. Then, the particle size and shell thickness were analyzed by optical microscope and inverted microscope, respectively. The ImageJ is the software that use to determine average diameter size and relative thickness (Thickness/ Outer radius).



(a) (b)

Figure 4.3 (a) Optical Microscope Image (4x) and (b) Inverted Microscope Image (20x) of 10wt% Epoxy Microcapsules which Synthesize with 1:1 of Core/shell Ratio and 1000 rpm of Agitaion Rate in a Coating Matrix



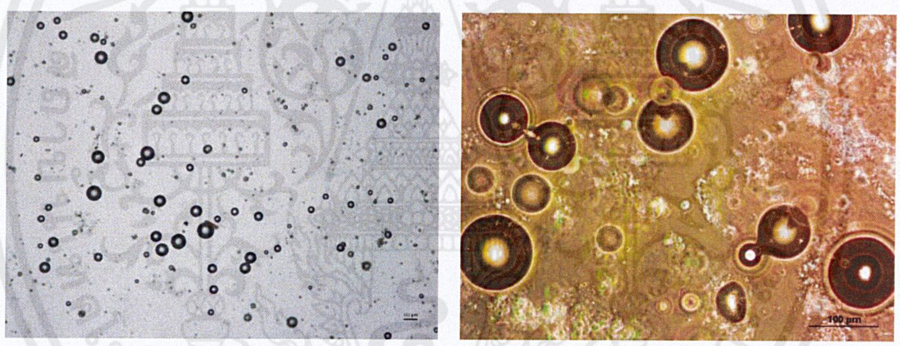
(a) (b)

Figure 4.4 (a) Optical Microscope Image (4x) and (b) Inverted Microscope Image (20x) of 10wt% Epoxy Microcapsules which Synthesize with 1:1 of Core/shell Ratio and 1500 rpm of Agitaion Rate in a Coating Matrix

The results show the epoxy microcapsules image (mixing of 10wt% epoxy microcapsules in coating matrix), which core/shell ratio is 1:1 and agitation rate are 1000 and 1500 rpm. From Figure 4.3 (b) and 4.4 (b) show the microcapsule component image, which consist of the dark edge part and light core part. In addition, it is observed the narrow edge joint between the dark part and light part. This result, confirms that the epoxy resin droplets are encapsulated by urea-formaldehyde polymer shell.

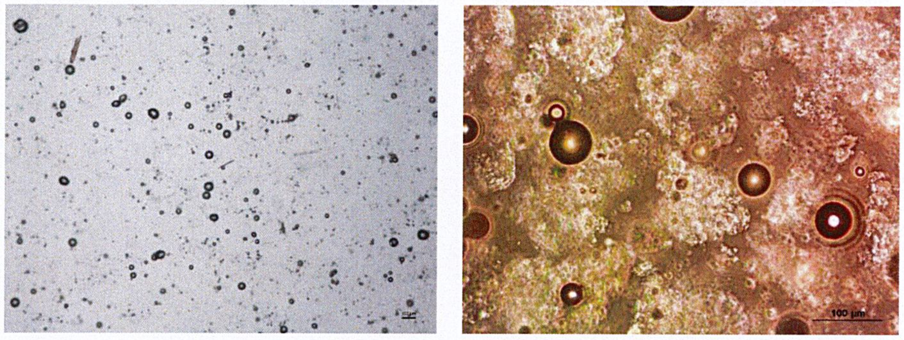
Comparison between Figure 4.3 and Figure 4.4, the average diameter sizes are 44.18 μm and 39.72 μm for 1000 and 1500 rpm, respectively. The relative thicknesses of both types are similar (Table 4.3). So, these results present that increasing agitation rate results in decreasing particle size and does not affect the shell thickness.

The other varying parameter is the ratio between core and shell in synthesized process. In the experiment, core/shell ratios are varied by the value of 1:1, 2:1, and 3:1, respectively.



(a) (b)

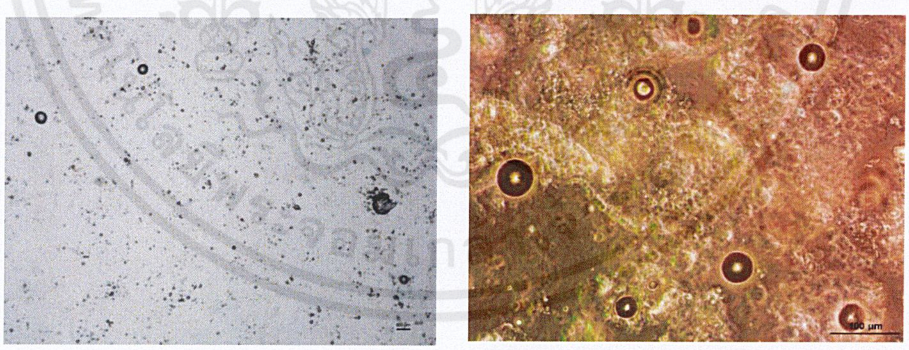
Figure 4.5 (a) Optical Microscope Image (4x) and (b) Inverted Microscope Image (20x) of 10wt% Epoxy Microcapsules which Synthesize with 2:1 of Core/shell Ratio and 1000 rpm of Agitaion Rate in a Coating Matrix



(a) (b)

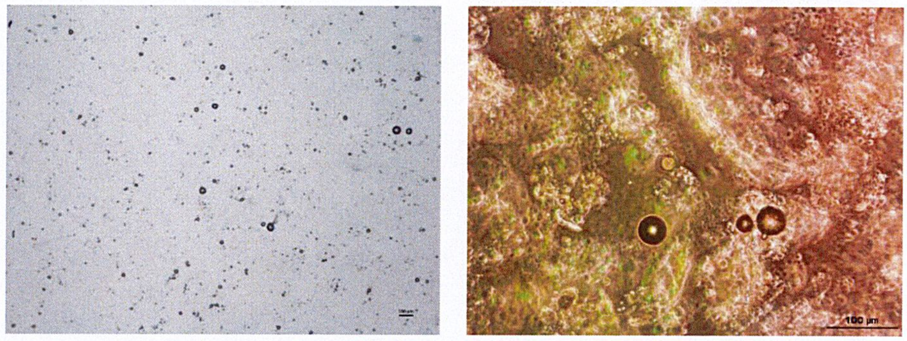
Figure 4.6 (a) Optical Microscope Image (4x) and (b) Inverted Microscope Image (20x) of 10wt% Epoxy Microcapsules which Synthesize with 2:1 of Core/shell Ratio and 1500 rpm of Agitaion Rate in a Coating Matrix

Comparison between Figure 4.4 and Figure 4.6, when the core/shell ratio was increased to 2:1, the average diameter size is similar to average diameter size of microcapsules which synthesized with 1:1 core/shell ratio. In addition, the relative thicknesses of both types are similar. So, it results that increasing core/shell ratio does not affect particle size and shell thickness.



(a) (b)

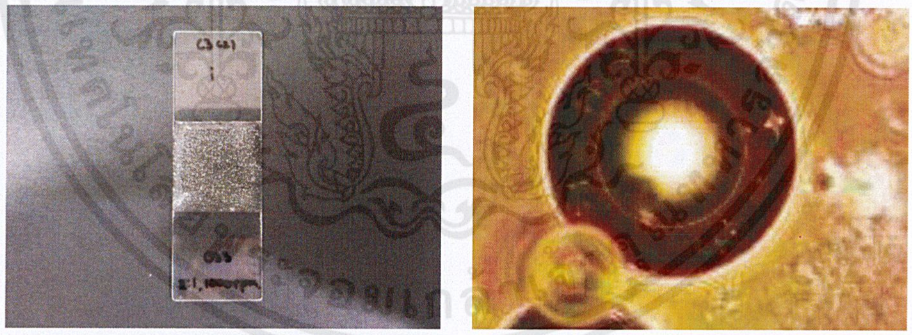
Figure 4.7 (a) Optical Microscope Image (4x) and (b) Inverted Microscope Image (20x) of 10wt% Epoxy Microcapsules which Synthesize with 3:1 of Core/shell Ratio and 1000 rpm of Agitaion Rate in a Coating Matrix



(a) (b)

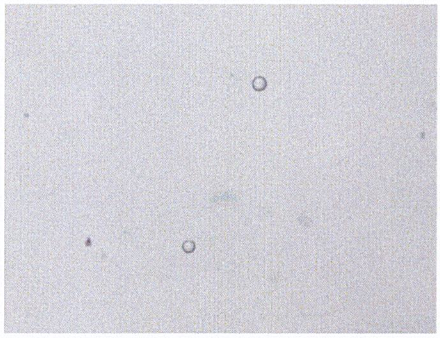
Figure 4.8 (a) Optical Microscope Image (4x) and (b) Inverted Microscope Image (20x) of 10wt% Epoxy Microcapsules which Synthesize with 3:1 of Core/shell Ratio and 1500 rpm of Agitaion Rate in a Coating Matrix

From the results in Figure 4.7 and Figure 4.8, when the core/shell ratio was increased to 3:1, the quantity of epoxy microcapsule seems to be decreased because increasing amount of liquid core (epoxy resin) results weak shell. As a result, the capsules were collapsed during drying process and coating process.

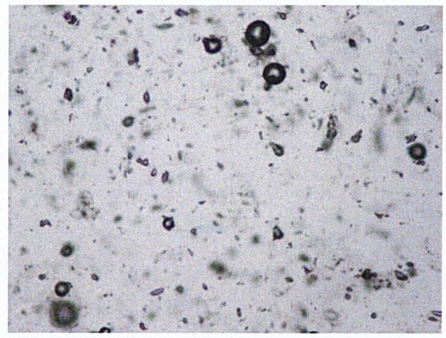


(a) (b)

Figure 4.9 The Images of (a) a Specimen of Epoxy Microcapsule distributed in Coating, and (b) a Single Epoxy Microcapsule Microcapsules which Synthesize with 2:1 of Core/shell Ratio and 1000 rpm of Agitaion Rate in Coating Matrix



(a)



(b)

Figure 4.10 Optical Microscope Images of (a) Bubbles of Coating Matrix, and (b) Hollow Urea-formaldehyde Capsules

Another result confirms that the epoxy microcapsules contain both epoxy resin (Core) and urea-formaldehyde (Shell). The Figure 4.10 shows the bubbles of coating matrix and hollow urea-formaldehyde. The bubbles have a light spherical shape which is obviously different from the epoxy microcapsules. The urea-formaldehyde capsules which are without the epoxy resin as a core have an uncertain shape. A few number of them are spherical shape which cannot observe a joint between a core and shell.

As a result, it clearly confirms that the synthesized epoxy microcapsules were contained epoxy resin (Core), which encapsulate in a urea-formaldehyde shell.

Table 4.3 Summary Table of Average Diameter Size and Relative Shell Thickness

Core/shell ratio		**Agitation rate (rpm)**	
		1000	**1500**
1:1	Average diameter size	44.18 μm	39.72 μm
	Relative shell thickness	0.41	0.40
2:1	Average diameter size	46.89 μm	39.19 μm
	Relative shell thickness	0.43	0.41
3:1	Average diameter size	N/A	N/A
	Relative shell thickness	N/A	N/A

4.3.2 Particle Size Distribution

After analyzing the particle size and shell thickness, the particle size distributions of epoxy microcapsules are concerned in this topic. The particle sizes were analyzed by using ImageJ. Then, the histogram plots is used to generate the distribution value (i.e., Standard deviation) by using Microsoft Excel software. In this study, the epoxy microcapsules which are 3:1 Core/Shell cannot determine the distribution. Because they collapse during drying and coating process, it has too less data to generate the accuracy distribution plot.

1) Particle Size Distributions of Epoxy microcapsules

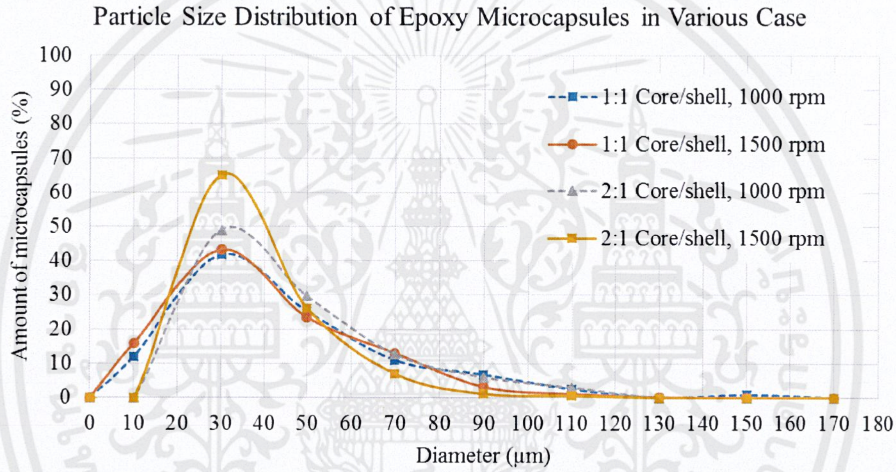


Figure 4.11 Particle Size Distribution of Epoxy Microcapsules in Various Cases

The Particle Size Distributions of 10wt% Epoxy microcapsules in coating matrix were show in Figure 4.11. They are the relation between the amount of microcapsules and a diameter. The Table 4.4 shows the standard deviation of the distribution plot in each case. A comparison of particle size distributions in each case will describe in the next topic.

Table 4.4 The Standard Deviation of Particle Size Distribution

Core/shell ratio	Standard deviation (SD)	
	1000 rpm	1500 rpm
1:1	25.54	21.82
2:1	21	14.57

2) Particle Size Distribution of Epoxy Microcapsules with Different Agitation Rate

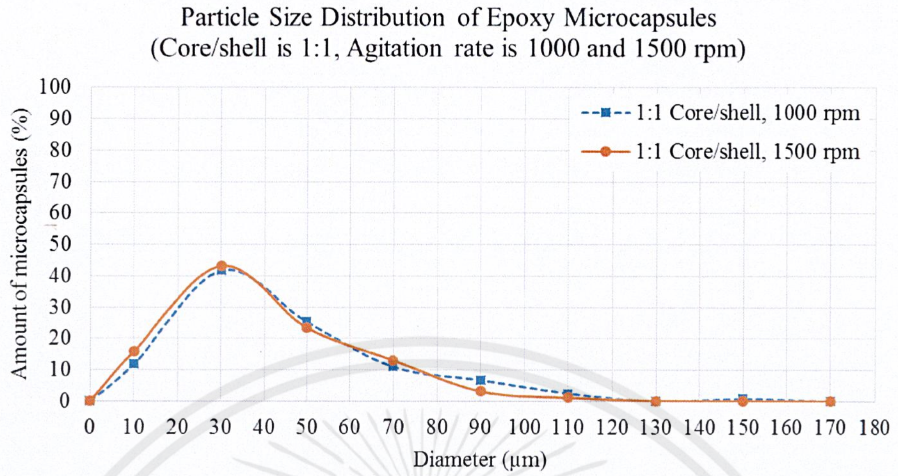


Figure 4.12 Particle Size Distribution of Epoxy Microcapsules which Synthesize with 1:1 of Core/shell Ratio

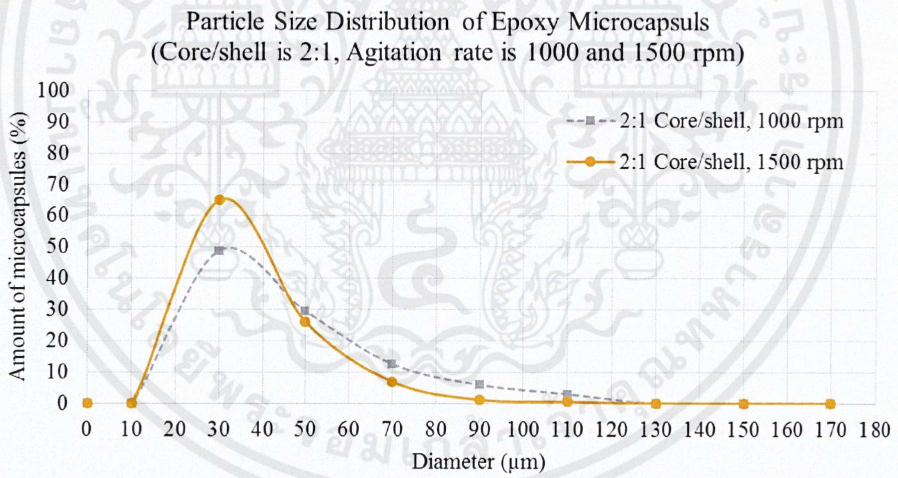


Figure 4.13 Particle Size Distribution of Epoxy Microcapsules which Synthesize with 2:1 of Core/shell Ratio

When define the constant core/shell ratio, increasing agitation rate results in more narrow size distribution. Obviously resulting in the core/shell ratio is 2:1, the distribution value of particle size distribution which synthesize in different agitation rate is more different than the distribution which synthesize with 1:1 core/shell ratio.

Then, the effect of core/shell ratio to the particle size distribution is studied by fixed the agitation rate and vary core/shell ratio

3) Particle Size Distribution of Epoxy Microcapsules with Different Core/Shell Ratio

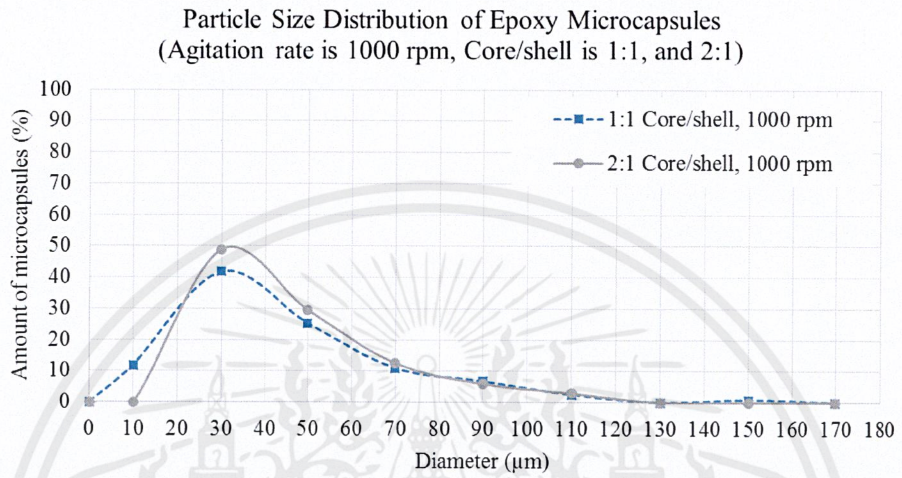


Figure 4.14 Particle Size Distribution of Epoxy Microcapsules which Synthesize with 1000 rpm of Agitation rate

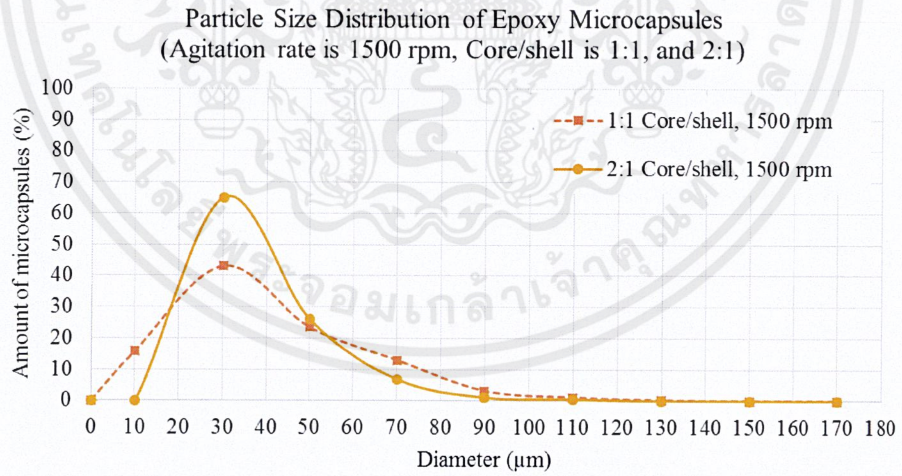


Figure 4.15 Particle Size Distribution of Epoxy Microcapsules which Synthesize with 1500 rpm of Agitation rate

When define the constant agitation rate, increasing core/shell ratio results more narrow size distribution. Obviously resulting in the agitation rate is 1500 rpm, the distribution value of particle size distribution which synthesize in core/shell ratio is more different than the distribution which synthesize with 1000 rpm of agitation rate.

Hence, in order to achieve the narrow or broad size distribution, the agitation rate and the core/shell ratio must be concerned. The narrow size distribution is achieved with high agitation rate and core/shell ratio.

Table 4.5 Summary Table of the Effect of Varying Parameters on Dependent Parameters

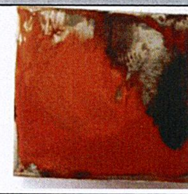
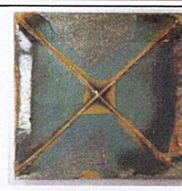
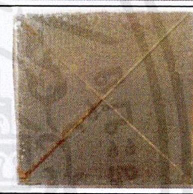
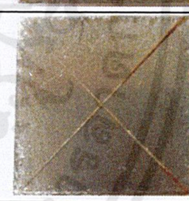
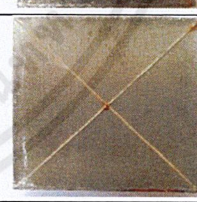
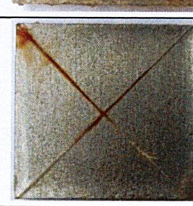
Dependent parameters	Varying parameters	
	Agitation rate	Core/shell ratio
1. Particle size	[+,-]	N/A
2. Shell thickness	N/A	N/A
3. Particle size distribution (Standard deviation)	[+,-]	[+,-]
4. Particle formation	[+,+]	[+,-]
5. Surface morphology (Roughness)	[+,+]	[+,+]

Note: 1) [Varying parameters, Dependent parameters]
2) (+) is increasing and (-) is decreasing
3) N/A is no effect

4.4 A Quick Test of Corrosion Resistance to Access Self-healing Ability

For testing anti-corrosion, a steel test piece was coated with a thin layer of coating embedded with various epoxy microcapsule and was immersed in 3.5wt% sodium chloride for 7 days. After that characterize a self-healing ability as a corrosion resistance.

Table 4.6 Surface of Steel Test Pieces after 7 Days Immersion

Sample	Surface images
1. Blank sample (Without coating)	
2. Coating without epoxy microcapsule	
3. Coating embedded with epoxy microcapsules which synthesize with 1:1 of core/shell ratio and 1000 rpm of agitation rate	
4. Coating embedded with epoxy microcapsules which synthesize with 1:1 of core/shell ratio and 1500 rpm of agitation rate	
5. Coating embedded with epoxy microcapsules which synthesize with 2:1 of core/shell ratio and 1000 rpm of agitation rate	
6. Coating embedded with epoxy microcapsules which synthesize with 2:1 of core/shell ratio and 1500 rpm of agitation rate	
7. Coating embedded with epoxy microcapsules which synthesize with 3:1 of core/shell ratio and 1000 rpm of agitation rate	
8. Coating embedded with epoxy microcapsules which synthesize with 3:1 of core/shell ratio and 1500 rpm of agitation rate	

After a steel test piece was coated with a thin layer of coating embedded with various epoxy microcapsule and was immersed into 3.5wt% sodium chloride for 7 days. The rust occurred on the surface of the steel by various quantities in various case. Compare with different agitation rate, the higher agitation rate provide less rust than lower agitation rate. For different core/shell ratios, the quantity of rust of the higher core/shell ratio provide less rust than lower core/shell ratio. Moreover, the coating embedded with epoxy microcapsules synthesized by 3:1 of core/shell ratio has low ability of anti-corrosion.

As a result, the coatings embedded with epoxy microcapsule which synthesized with 2:1 of core/shell ratio and 1500 of agitation rate have highest corrosion resistance due to self-healing behavior on the scratch area. The second corrosion resistance is the coatings embedded with epoxy microcapsule which synthesized with 2:1 of core/shell ratio and 1000 of agitation.

CHAPTER V
CONCLUSIONS

5.1 Suitable Epoxy Microcapsule for Development of Self-healing Coating

The microencapsulation of epoxy microcapsules was prepared by varying parameters including agitation rate and core/shell ratio which affect particle formation, surface morphology, particle size, shell thickness, and particle size distribution. To apply the microcapsules in an application of self-healing coating, it is necessary to study these effects. The particles should be small and strong to provide good mechanical properties to the coating, however if the surface of the particle is too rigid it will be difficult for the liquid core to flow out of the capsule to heal the coating. Also narrow particle size distribution of particles is preferred so that the property of the microcapsule would be uniform.

1) Chemical Structure Analysis

The Fourier Transform Infrared Spectrum can predict that the epoxy microcapsules consist of commercial epoxy resin and urea-formaldehyde.

2) Characteristic of Particle Formation and Surface Morphology

The particle formation of the microcapsules is proportional to agitation rate, higher agitation rate provides a good formation. Increasing of core/shell ratio results the weak polymer shell which cannot exist on the coating matrix. The roughness surface morphology was increased by increase the agitation rate or increase core/shell ratio.

3) Particle Size and Shell Thickness Analysis

The agitation rate is inverted proportional to a particle size and does not affect the shell thickness. While, the core/shell ratio does not affect both a particle size and a shell thickness. Furthermore, increasing agitation rate or core/shell ratio provide more narrow size distribution.

Hence, to apply the microcapsules in an application of self-healing coating, the optimum agitation rate should be high. The core/shell ratio should be moderate; too low core/shell ratio provides stronger polymeric shell but too high core/shell ratio provides weaker polymeric shell.

4) Quick Test of Corrosion Resistance to Access Self-healing Ability

A steel test piece which is coated with a thin layer of coating embedded with epoxy microcapsule synthesized with 2:1 core/shell ratio and 1500 agitation rate has highest corrosion resistance due to self-healing behavior on the scratch area.

5.2 Recommendation

5.2.1 In order to achieve in higher corrosion resistance, the microcapsules can be extended by apply with coating such as embedded with excess hardener system, catalyst, or hardener microcapsule.

5.2.2 The commercial system is a difficult system to study. It need to have more experimental work to be success such as the reliable of a chemical structure, and a chemical and physical properties.

5.2.3 A healing ability or a corrosion resistance of a self-healing coating based on microencapsulation should be measure by specific measurement such as Electrochemical Impendence Spectroscopy (EIS).

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APPENDIX

APPENDIX A

ANALYTICAL EQUIPMENT

A.1 Fourier Transform Infrared Spectroscopy [30]

In many ways, mid-infrared spectroscopy would appear to be the ideal technology for on-line chemical analysis. After all, IR spectroscopy is the only analytical method which provides both ambient temperature operation and the ability to directly monitor the vibrations of the functional groups which characterize molecular structure and govern the course of chemical reactions.

Light from the light source is directed to the beam splitter. Half of the light is reflected and half is transmitted. Then, the reflected light goes to the fixed mirror where it is reflected back to the beam splitter. The transmitted light is sent to the moving mirror and is also reflected back towards the mirror. At the beam splitter, each of the two beams (from the fixed and moving mirrors) are split into two: one goes back to the source (and "lost" since it does not reach the detector) and the other goes towards the detector. Hence the detector sees two beams: one from the moving mirror and the other from the fixed mirror. The two beams reaching the detector come from the same source and have an optical path difference determined by the positions of the two mirrors, i.e. they have a fixed phase difference. Therefore the two beams interfere. The two beams may be made to interfere constructively or destructively for a particular frequency by positioning the moving mirror. If the moving mirror is scanned over a range a sinusoidal signal will be detected for that frequency, with its maximum corresponding to constructive interference and the minimum corresponding to destructive interference. This sinusoidal signal is called interferogram. Then a corresponding spectrum frequency against intensity plot is computed using Fourier transform.

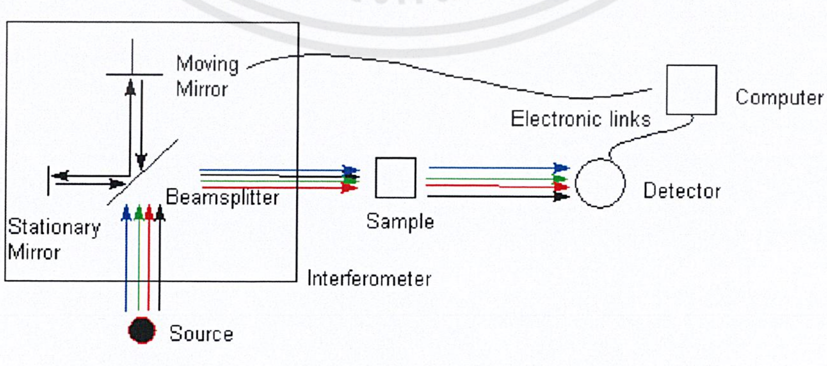

Figure A.1.1 The Composition of FTIR Spectroscopy

A.2 Scanning Electron Microscope [31]

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques. The SEM is also capable of performing analyses of selected point locations on the sample.

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light and heat.

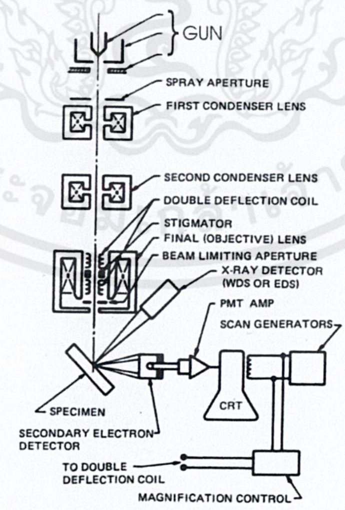

Figure 1.11. Schematic drawing of the electron and x-ray optics of a combined SEM–EPMA.

Figure A.2.1 The Composition of Scanning Electron Microscope

A.3 Optical Microscope and Inverted Microscope [32]

The compound microscope uses a set of many lenses in order to maximize magnification. The microscopes components have objective and eyepiece assemblies. These multi-component lenses are designed to reduce aberrations, particularly chromatic aberration and spherical aberration. In modern microscopes the mirror is replaced by a lamp unit providing stable, controllable illumination

Compound optical microscopes are typically used to examine a smear, a squash preparation, or a thinly sectioned slice of some material. With a few exceptions, they utilize light passing through the sample from below and special techniques are usually necessary to illuminate the sample to increase the contrast in the image to useful levels.

A common use of non-transmitted lighting is to study the thin structure of metals and minerals, where the light is reflected from the examined surface. The light is fed down through the objective using a semi-transparent mirror, and the reflected light observed as normal.

An inverted microscope is essentially an upside-down 'upright' life science microscope. This kind of microscope views objects from an inverted position than that of regular microscopes and are widely used in the study of cell cultures in liquid, since the "flat" part of a liquid sample will be the base of the liquid.

(a) (b)

Figure A.3.1 The Image of (a) Optical Microscope and (b) Inverted Microscope

APPENDIX B
FOURIER TRANSFORM INFRARED SPECTROSCOPY RESULTS

B.1 Fourier Transform Infared Spectrum of Epoxy Resin.

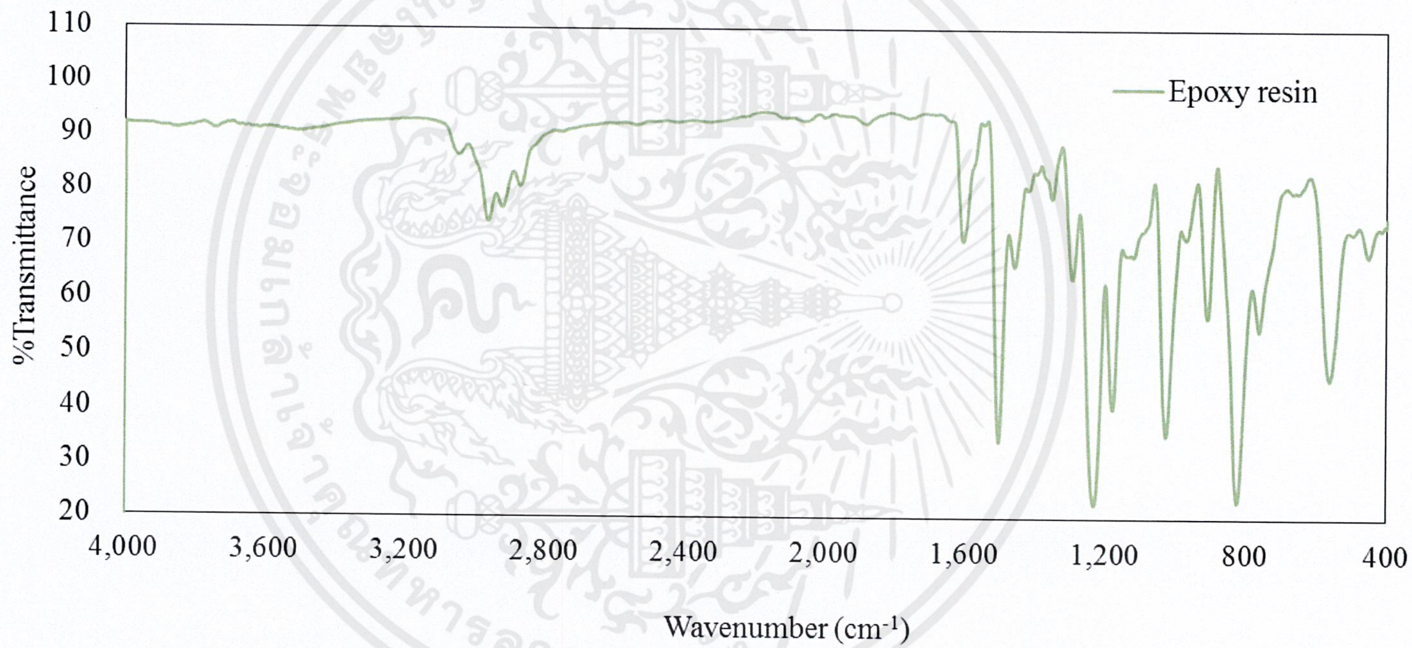

Figure B.1.1 Fourier Transform Infrared Spectrum of Epoxy Resin

B.2 Fourier Transform Infared Spectrum of Urea-formaldehyde.

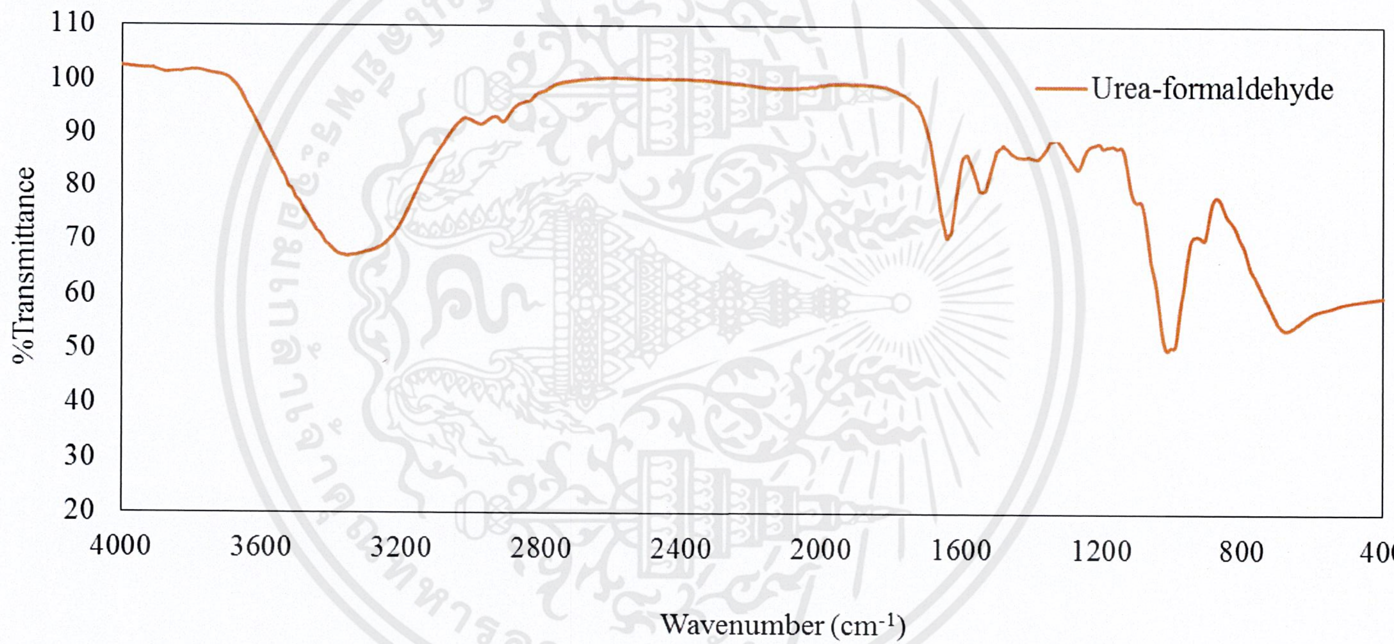

Figure B.2.2 Fourier Transform Infrared Spectrum of Urea-formaldehyde

B.3 Fourier Transform Infared Spectrum of Epoxy Microcapsules.

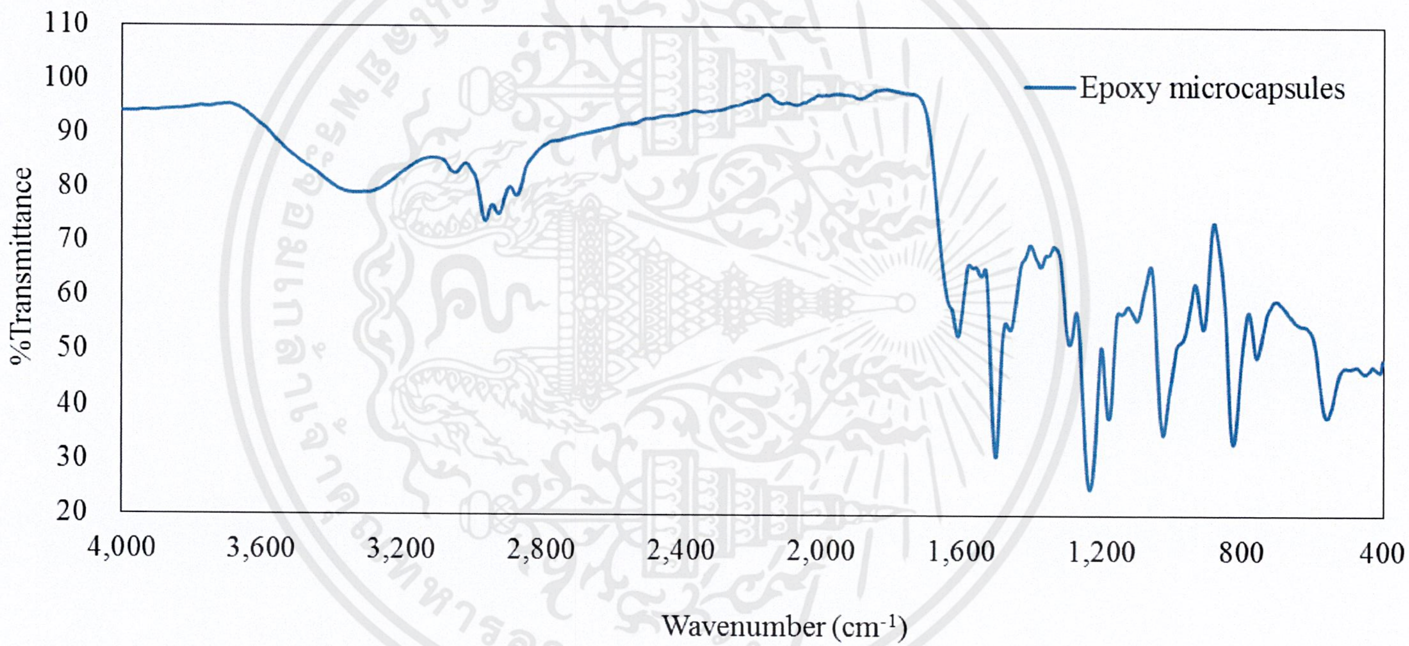

Figure B.3.1 Fourier Transform Infrared Spectrum of Epoxy Microcapsules

APPENDIX C
SCANNING ELECTRON MICROSCOPE RESULTS

C.1 SEM Image of Epoxy Microcapsules
(1:1 Core/Shell Ratio and 1000 rpm Agitation Rate)

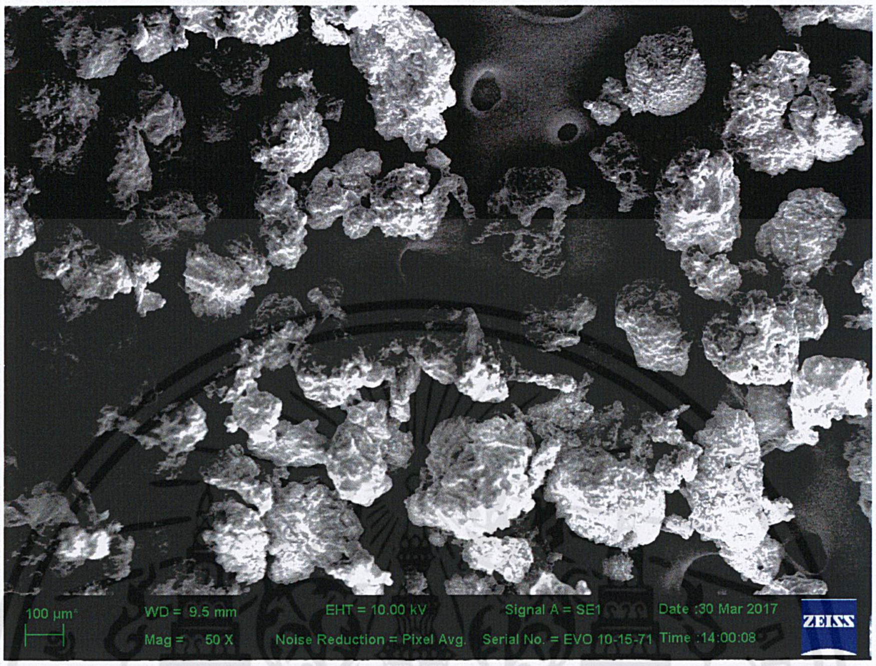

Figure C.1.1 1:1 Core/Shell Ratio and 1000 rpm Agitation Rate with 50x Magnitude

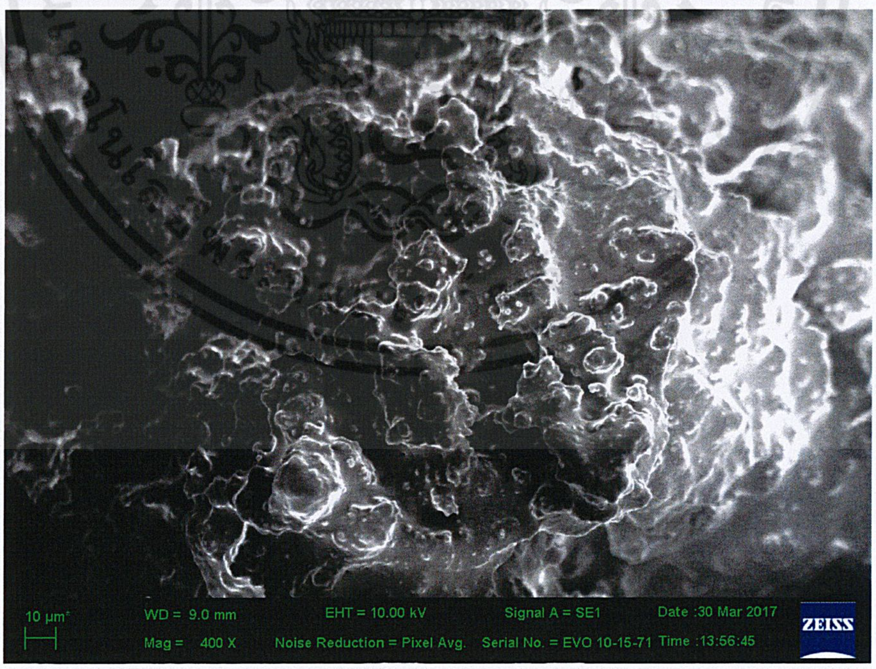

Figure C.1.2 1:1 Core/Shell Ratio and 1000 rpm Agitation Rate with 400x Magnitude

C.2 SEM Image of Epoxy Microcapsules
(1:1 Core/Shell Ratio and 1500 rpm Agitation Rate)

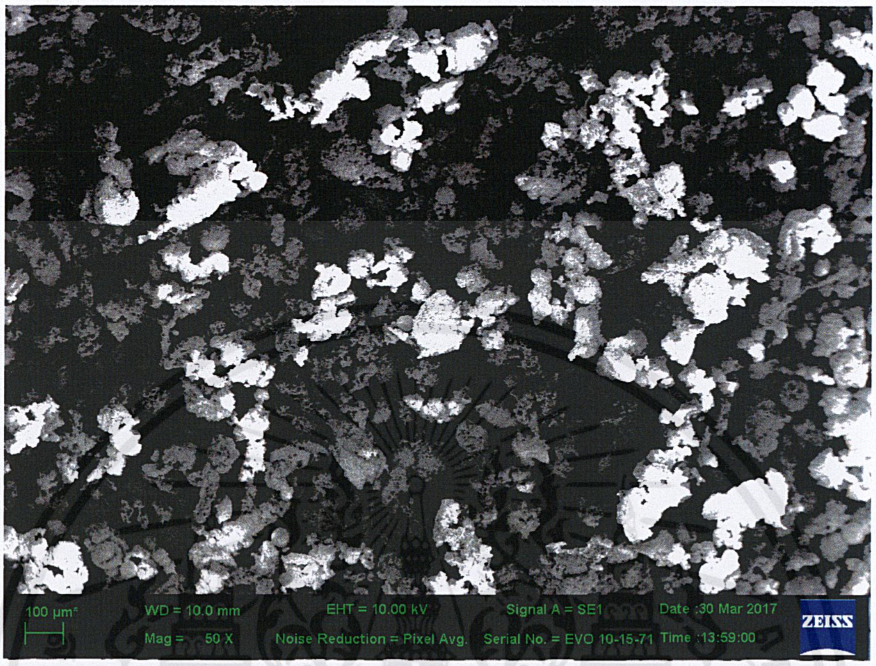

Figure C.2.1 1:1 Core/Shell Ratio and 1500 rpm Agitation Rate with 50x Magnitude

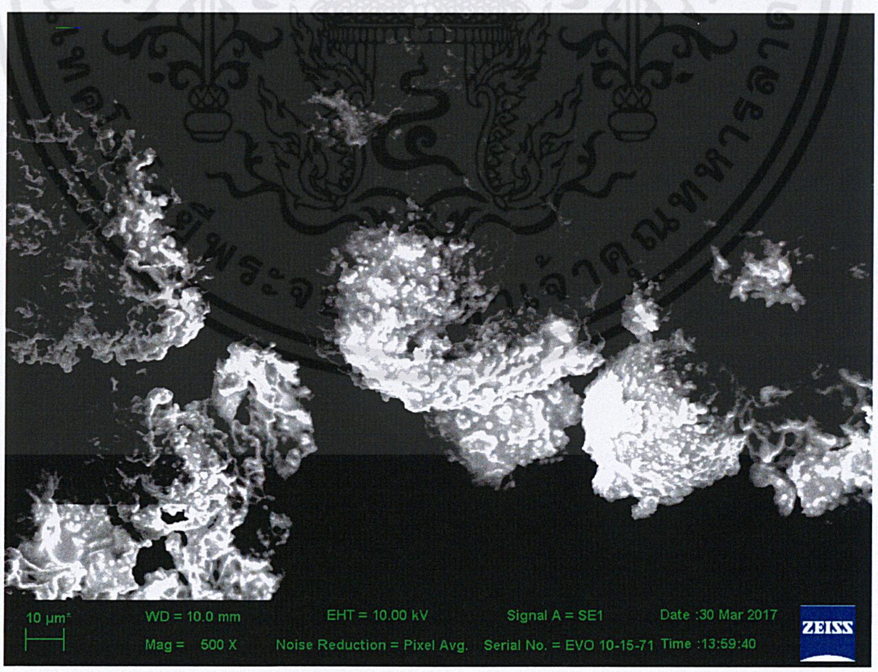

Figure C.2.2 1:1 Core/Shell Ratio and 1500 rpm Agitation Rate with 500x Magnitude

C.3 SEM Image of Epoxy Microcapsules
(2:1 Core/Shell Ratio and 1000 rpm Agitation Rate)

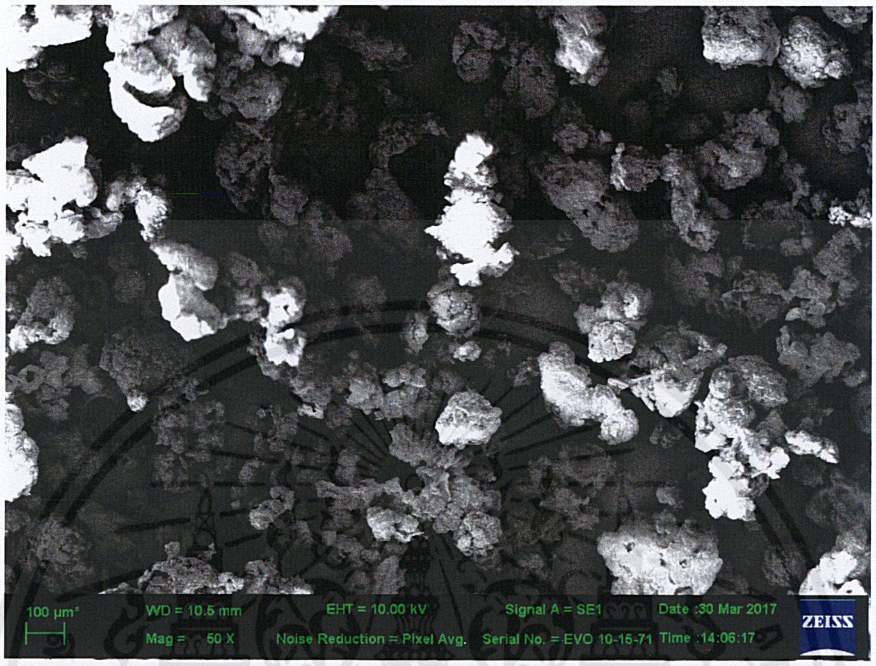

Figure C.3.1 2:1 Core/Shell Ratio and 1000 rpm Agitation Rate with 50x Magnitude

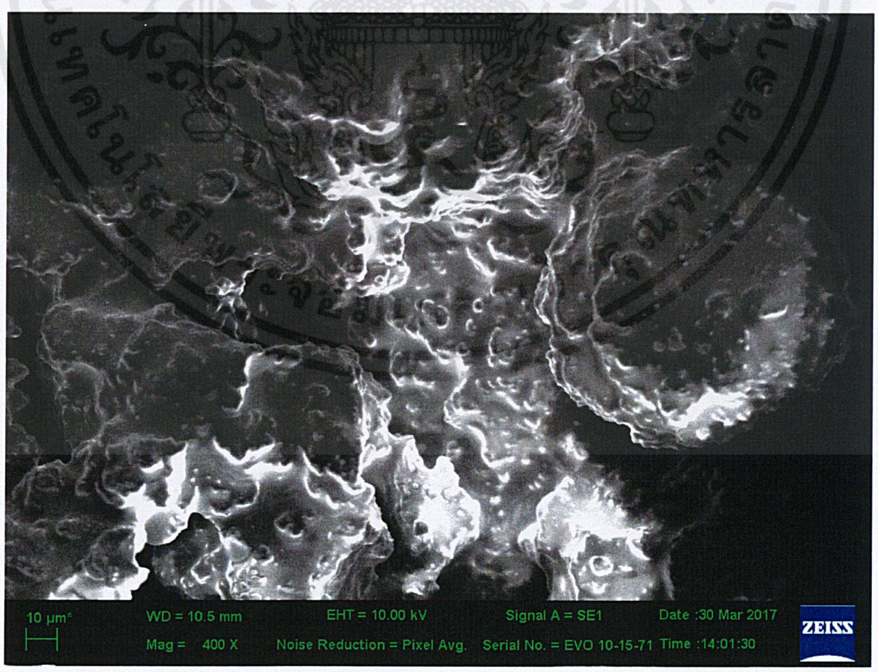

Figure C.3.2 2:1 Core/Shell Ratio and 1000 rpm Agitation Rate with 400x Magnitude

C.4 SEM Image of Epoxy Microcapsules
(2:1 Core/Shell Ratio and 1500 rpm Agitation Rate)

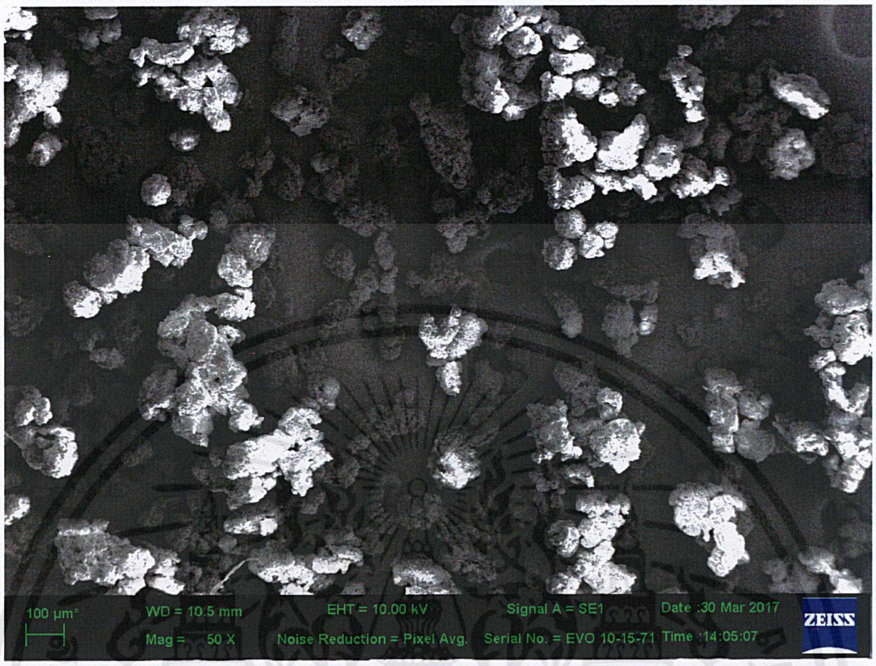

Figure C.4.1 2:1 Core/Shell Ratio and 1500 rpm Agitation Rate with 50x Magnitude

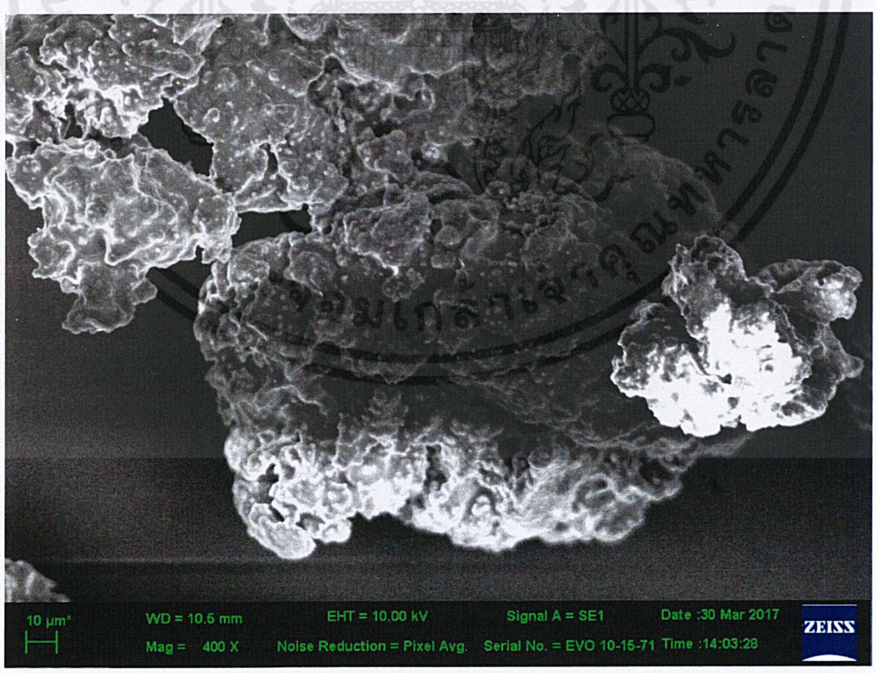

Figure C.4.2 2:1 Core/Shell Ratio and 1500 rpm Agitation Rate with 400x Magnitude

C.5 SEM Image of Epoxy Microcapsules

(3:1 Core/Shell Ratio and 1000 rpm Agitation Rate)

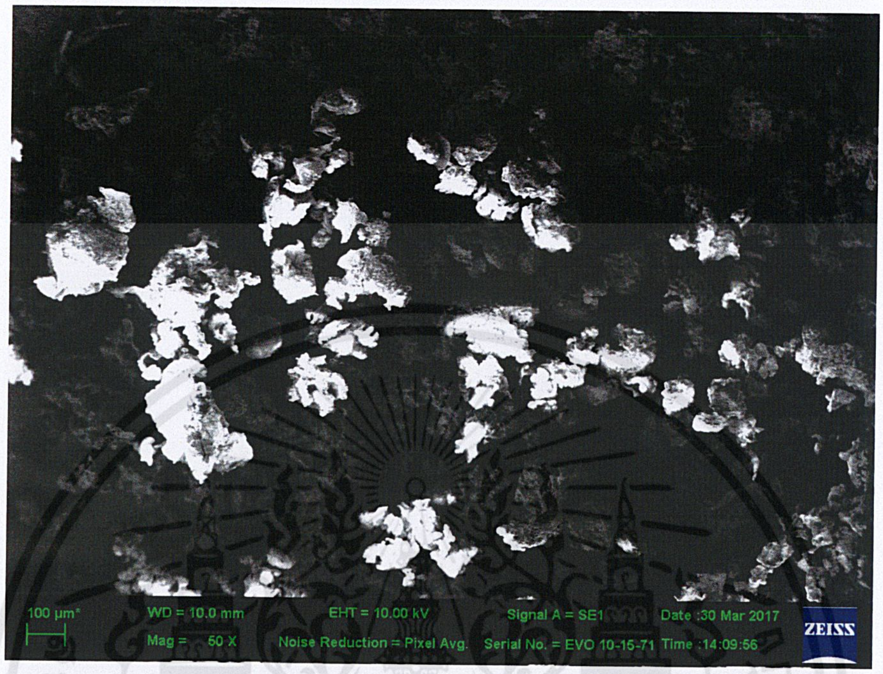

Figure C.5.1 3:1 Core/Shell Ratio and 1000 rpm Agitation Rate with 50x Magnitude

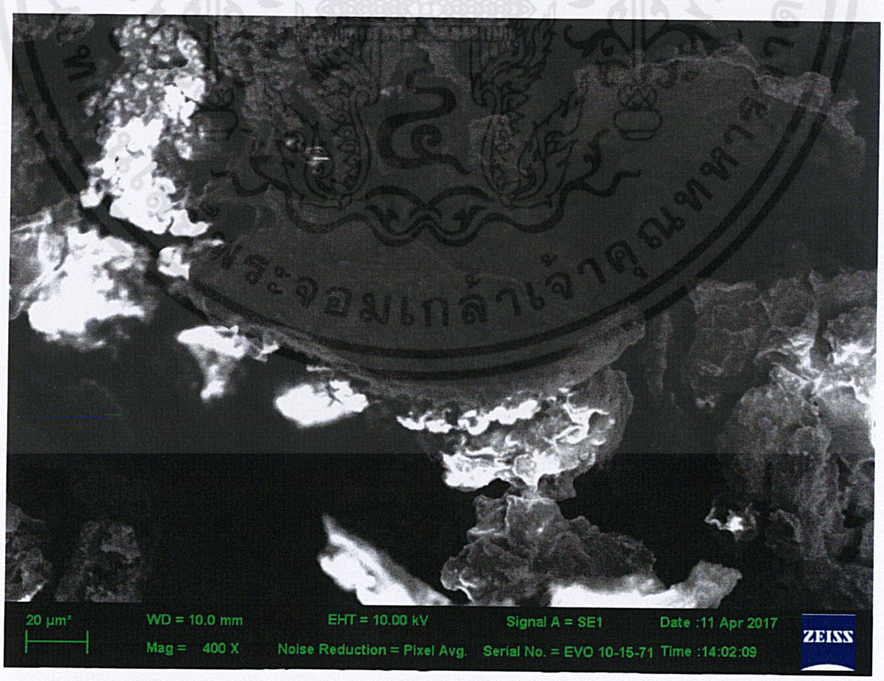

Figure C.5.2 3:1 Core/Shell Ratio and 1000 rpm Agitation Rate with 400x Magnitude

C.6 SEM Image of Epoxy Microcapsules
(3:1 Core/Shell Ratio and 1500 rpm Agitation Rate)

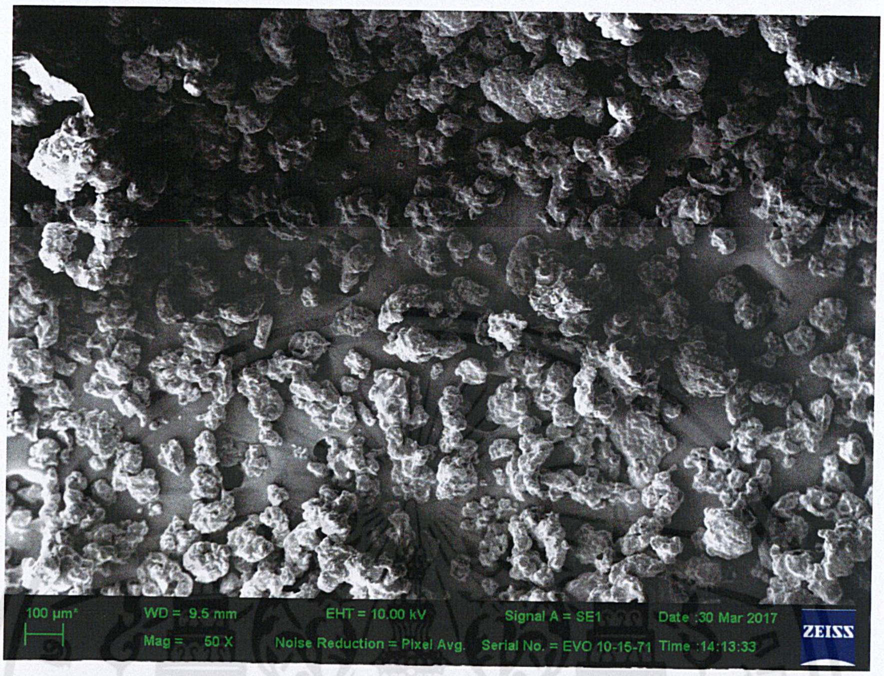

Figure C.6.1 3:1 Core/Shell Ratio and 1500 rpm Agitation Rate with 50x Magnitude

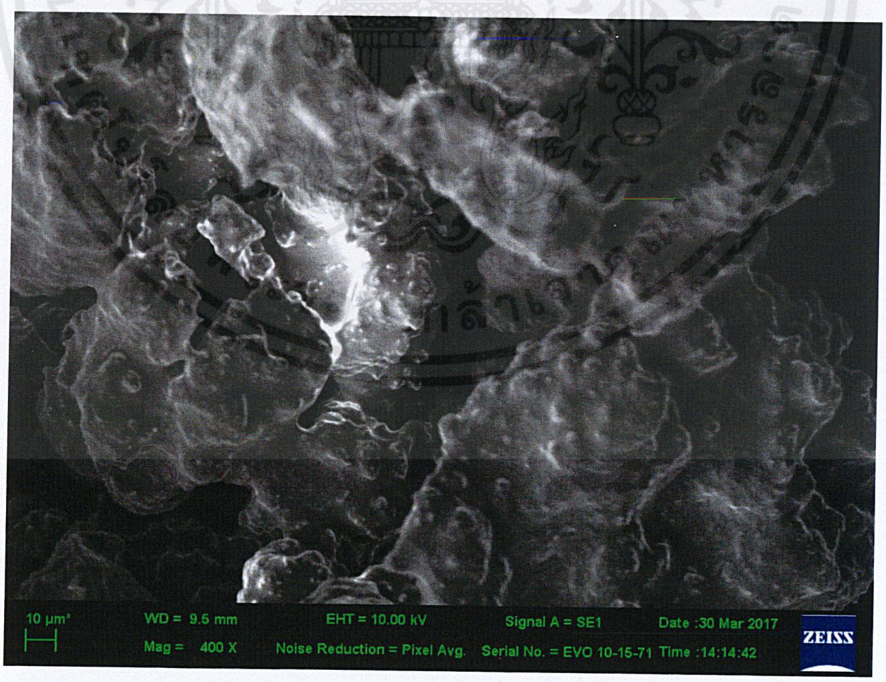

Figure C.6.2 3:1 Core/Shell Ratio and 1500 rpm Agitation Rate with 400x Magnitude

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