ไมโครเอนแคปซูเลชันของวัสดุเปลี่ยนสถานะด้วยซิลิกาจากโซเดียมซิลิเกตโดยกระบวนการอบแห้งแบบพ่นฝอย

นางสาวใฝ่ฝัน เสาวภา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2554

Microencapsulation of Phase Change Material with Silica from Sodium Silicate by Spray Drying Process

Miss Phaiphan Saowapa

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2011

Thesis Title	Microencapsulation of Phase Change Material with Silica from Sodium Silicate by Spray Drying Process
By	Miss Phaiphan Saowapa
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Apinan Soottitantawat, D.Eng.
Thesis Co-advisor	Wiyong Kangwansupamonkon, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………..….................Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

…………………………………….Chairman
(Assistant Professor Anongnat Somwangthanaroj, Ph.D.)

……………………………………..Thesis Advisor
(Assistant Professor Apinan Sootitantawat, D.Eng.)

……………………………………..Thesis Co-advisor

(Wiyong Kangwansupamonkon, Ph.D.)

……………………………………..Examiner
(Associate Professor Tawatchai Charinpanitkul, D.Eng.)

……………………………………..Examiner
(Assistant Professor Varong Pavarajarn, Ph.D.)

…………....………………………External Examiner

(Kritapas Laohhasurayotin, Ph.D.)

ใฝ่ฝัน เสาวภา : ไมโครเอนแคปซูเลชันของวัสดุเปลี่ยนสถานะด้วยซิลิกาจากโซเดียมซิลิเกตโดยกระบวนการอบแห้งแบบพ่นฝอย (MICROENCAPSULATION OF PHASE CHANGE MATERIAL WITH SILICA FROM SODIUM SILICATE BY SPRAY DRYING PROCESS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.อภินันท์ สุทธิธารธวัช, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.วิยงค์ กังวานศุภมงคล, 82 หน้า.

วัสดุเปลี่ยนสถานะคือวัสดุที่สามารถดูดความร้อน กักเก็บความร้อนและคายความร้อนได้เมื่อเปลี่ยนสถานะ เพื่อรักษาสมบัติของวัสดุเปลี่ยนสถานะและแก้ปัญหาการรั่วไหลของวัสดุเปลี่ยนสถานะ จึงมีการพัฒนาการกักเก็บวัสดุเปลี่ยนสถานะ ในงานวิจัยนี้ศึกษาการกักเก็บวัสดุเปลี่ยนสถานะคือสารนอมอล-ออกตาเดคเคนด้วยซิลิกาซึ่งเป็นวัสดุที่มีความเสถียรทางเคมีและมีความแข็งแรง โดยเตรียมซิลิกาจากโซเดียมซิลิเกตซึ่งเป็นสารตั้งต้นที่มีราคาถูกกว่าเตตระเอทิลออร์โทซิลิเกต ไมโครแคปซูลของสารนอมอล-ออกตาเดคเคนด้วยซิลิกาเตรียมจากอิมัลชันชนิดน้ำมันในน้ำซึ่งมีสารนอมอล-ออกตาเดคเคนเป็นวัฏภาคน้ำมันและสารละลายโซล-เจลของสารโซเดียมซิลิเกตซึ่งเป็นสารห่อหุ้มเป็นวัฏภาคน้ำ และมีการใช้สารทวีน 20 เป็นอิมัลซิฟายเออร์ จากนั้นนำอิมัลชันที่ได้มาผ่านเครื่องอบแห้งแบบพ่นฝอยจะได้ไมโครแคปซูลของวัสดุเปลี่ยนสถานะ จากการศึกษาพบว่าการเตรียมไมโครแคปซูลจากเตรียมอิมัลชันที่ความเร็วรอบ 18,000 รอบต่อนาที เวลาในการปั่นกวน 3 นาที ปริมาณของวัสดุเปลี่ยนสถานะร้อยละ 50 โดยน้ำหนักของแข็งทั้งหมด และอัตราส่วนโดยโมลของสารลดแรงตึงผิวต่อวัสดุเปลี่ยนสถานะ คือ 0.1:1 เป็นสภาวะที่ไมโครแคปซูลมีค่าการดูดคายความร้อนมากที่สุด ไมโครแคปซูลที่ได้เป็นผงแห้ง มีลักษณะเป็นทรงกลม กลวง ผิวเรียบ มีวัสดุเปลี่ยนสถานะกระจายตัวอยู่บนผนังของอนุภาคซิลิกา โดยปริมาณของวัสดุเปลี่ยนสถานะที่ถูกกักเก็บในไมโครแคปซูลประมาณร้อยละ 7.8 โดยน้ำหนักของแข็งทั้งหมด และปริมาณของวัสดุเปลี่ยนสถานะที่คงเหลืออยู่ภายในไมโครแคปซูล เมื่อเทียบกับปริมาณวัสดุเปลี่ยนสถานะที่เติมลงไปในการเตรียมอิมัลชันประมาณร้อยละ 19 โดยไมโครแคปซูลมีค่าการดูด และคายความร้อนของโดยเฉลี่ย คือ 14.85 จูลต่อกรัม

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

5370464721: MAJOR CHEMICAL ENGINEERING
KEYWORDS: PHASE CHANGE MATERIAL/ MICROENCAPSULATION/ SPRAY DRYING

PHAIPHAN SAOWAPA: MICROENCAPSULATION OF PHASE CHANGE MATERIAL WITH SILICA FROM SODIUM SILICATE BY SPRAY DRYING PROCESS, ADVISOR: ASST. PROF. APINAN SOOTTITANTAWAT, D.Eng., CO-ADVISOR: WIYONG KANGWANSUPAMONKON, Ph.D., 81 pp.

Phase change materials (PCMs) are substance that absorb, store, and release heat when they change state. In order to protect the PCMs from surrounding, to maintain the amount of them and their ability and to avoid the leakage of melted PCMs, the PCMs were encapsulated. Silica has many desirable properties for using as a shell material to encapsulate PCMs such as chemical inertness, high mechanical strength. Efforts have been devoted to reduce the cost of encapsulation PCMs with silica by using low cost sodium silicate as a silica source to replace the tetraethyl orthosilicate (TEOS). The encapsulated PCMs with silica as a supporting material was successfully prepared in O/W emulsion. The encapsulation efficiency and stability of the capsule depends on the emulsion preparation. In this research, the O/W emulsion for preparing the microencapsulation of PCMs with silica from sodium silicate by spray drying was studied. The microcapsules were prepared in an O/W emulsion with Tween 20 as emulsifier. The oil phase was n-Octadecane as the model of PCM. The water phase is the silica sol-gel solution which was formed via sol-gel reaction of sodium silicate solution with hydrochloric acid. Finally, the microcapsules were obtained by spray drying of an emulsion. The optimum condition for preparing microcapsule as following: the homogenizing speed 18,000 rpm homogenizing time 3 minutes phase change material 50 wt% of total solid and mole ratio of surfactant and phase change material 0.1:1. The spray dried microcapsules were smooth and nonporous spherical particle containing PCMs droplets which were embedded in the wall of the silica particles. Encapsulation efficiency and retention of phase change material in microcapsule were 7.8% and 19%, respectively. The average latent heat of microencapsulated n-Octadecane was 14.85 J/g.

Department: Chemical Engineering Student's Signature

Field of Study: Chemical Engineering Advisor's Signature

Academic Year: 2011 Co-advisor's Signature

ACKNOWLEDGEMENTS

I would like to express my gratitude to the following institutes and persons, for their support and guidance throughout the research.

To my advisor, Assistant Professor Dr. Apinan Sootitantawat and my co-advisor, Dr. Wiyong Kangwansupamonkon for their guidance, help, kindness, encouragement, forgiveness and time taken to read the manuscript.

To Assistant Professor Dr. Anongnat Somwangthanaroj as the chairman. Associate Professor Dr. Tawatchai Charinpanitkul, Assistant Professor Dr. Varong Pavarajarn and Dr. Kritapas Laohhasurayotin, members of the thesis committee for their kind cooperation, comment, and discussions.

To The Center of Excellent in Particle Technology Chulalongkorn University and all members for their good advice and assistance in providing convenience, chemicals and materials for my research.

To National Nanotechnology Center (NANOTEC) Thailand and staffs for their patience and help.

To National Nanotechnology Center (NANOTEC) Thailand for financial support.

To the Centennial Fund of Chulalongkorn University for financial support.

To my family and my friends for their love, support and encouragement throughout the study.

Last but not least, my thanks to all persons who have cooperated in one-way or another to bring about this thesis possible.

CONTENTS

Page

CHAPTER

CHAPTER Page

CHAPTER Page

LIST OF TABLES

Table Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION

The enlargement in the level of greenhouse gas emissions and the increasing in fuel prices are the main reason of effort to more effectively utilize various sources of renewable energy. One of the options is to develop energy storage devices, which are as important as developing new sources of energy. At present, thermal energy storage systems are essential for reducing dependency on the fossil fuels and then contributing to a more efficient environmental friendly energy use. Energy storage not only reduces the mismatch between supply and demand but also improves the performance and reliability of energy systems and plays an important role in conserving the energy [1]. The Phase Change Materials are well-known as a type of heat storage material since their great capacity to absorb store and release the latent heat involved in a phase change process, the phase change materials have received attention in many applications such as used in solar heating systems, cooling or heating in buildings, systems of waste heat and clothing because of their great capacity to absorb and slowly release the latent heat involved in a phase change process [2,3].

A variety of PCMs such as hydrated salts, paraffins waxes, organic, inorganic and fatty acids are well known for their thermal characteristics. The selection of the phase change material depends on their usage. For example, the phase change materials that melt under 5 °C are used to impart warmth to a skin of human under cold weather state, for the phase change materials that melt around 30 °C would be used in the clothes to make some feeling of freshness [4]. Many of phase change materials are available in any required temperature range. The chemical materials can be verified as a phase change materials from their attitude melting temperature and latent heat of fusion [5].

Due to the advantages of organic phase change materials such as good phase-change performance and good compatible with many materials so the organic phase change materials have appealed in a recent research. The one of organic phase change materials which is Paraffin waxes (n-alkanes) that have different melting temperature (T_m) and crystallization temperatures (T_c). The phase change temperature depends on the number of carbon atoms in their chains, the linear hydrocarbons can change phases in the temperature that making humans feel relaxed that is around 18–36 °C. n-Octadecane is a good performance phase change material that have a high latent heat is 241.2 J/g and its phase change temperature is in range 23–28 °C that is comfortable for the human body.

Although the PCMs have many good abilities, but are not easy to handle during use, because they have a leakage problem when undergoing solid–liquid phase-change processes [6]. Furthermore, The PCMs freezes on the heat exchanger surface resulting in a poor heat-transfer rate because of the paraffin wax exhibits low thermal conductivity. Many attempts have been made to overcome these difficulties. Recently, a new technique of utilizing microencapsulated PCM in energy storage system has been developed. There are many advantages of microencapsulated paraffin wax. First is preventing of reduction of the reactivity of the paraffin wax with the outside environment. Second is increasing the area for heat-transfer and to resist frequent changes in volume of the phase change material in a phase change process [7].

Nowadays, Microencapsulation can take place by a spray-drying, coating processes or chemical process such as coacervation, interfacial polymerization techniques, emulsion polymerization, in situ polymerization. Moreover, there are different compounds capable of becoming shell materials [8]. Organic polymeric materials have been used as the shell using two-step methods. These methods include core–shell templating, interfacial polymerization, and coacervation and spray drying. The main issues associated with the use of polymers as shell materials are their low thermal conductivity and undesirable residues such as formaldehyde. There have been many reports on the use of silica as the shell material of microcapsules the shell material because of silica has a much higher thermal conductivity and chemical stability than the polymeric materials. Various methods have been proposed for making silica shelled microcapsules. For instance, using sol-gel method in O/W emulsion system, the silica shell was formed via hydrolysis and condensation from tetraethyl orthosilicate (TEOS) as a precursor with acetate acid as catalyst and the another method is prepare from an emulsion templating using sodium silicate as the precursor with NH_4HCO_3 as precipitant. Despite the use of different silica precursors and synthesis conditions, these methods have some similarities. The syntheses are carried out in two steps in batch reactors and involve the use of surfactants, and addition of acid [9-11]. In addition, Efforts have been to decrease the cost of encapsulation PCMs with silica, the encapsulation PCMs with silica by using low cost sodium silicate as a silica source to replace tetraethyl orthosilicate (TEOS) was prepared via hydrolysis and condensation from low-cost sodium silicate solution with Hydrochloric acid as a catalyst and ammonium bicarbonate as neutralizing agent [12]. Moreover, Microencapsulation of phase change material with silica by spray drying was studied. The microcapsules were successfully prepared in emulsion of n-Octadecane and methyl palmitate with silica sol that prepared from tetraethyl orthosilicate (TEOS) as a silica source and HCl acid as a catalyst, after that the emulsion was spray dried. The microcapsules were spherical shape and capable of thermal energy storage [13].

In this study, the preparation of the silica microcapsules containing *n*-Octadecane via a sol-gel using sodium silicate as a precursor by spray drying process was investigated. The aims of this research are to obtain the microcapsules which have good properties for used as the energy storage materials such as high thermal conductivity, high amount of latent heat and easy to handle and to reduce the cost of silica preparation by using sodium silicate as a silica source instead of tetraethyl orthosilicate (TEOS). The effects of the silica shell materials on microstructures, phase-change behaviors, and properties of the microencapsulated n-Octadecane are also investigated.

Objective

The objectives of this research are to prepare the microencapsulated phase change material with silica by spray drying using sodium silicate as a precursor.

Scope of the research

The microencapsulation in this research was prepared by sol-gel method according to the procedure reported by Chunyan, et al [12] before spray drying. First, the mixture which containing the phase change materials and surfactant was prepared. The silica sol was prepared by the reaction of Sodium silicate solution with Hydrochloric acid to form a silica gel. After that the silica sol was added into the mixture and then agitated by a homogenizer. The oil in water emulsion which the oil phase was n-Octadecane as the model PCM and the water phase was the silica sol-gel solution was obtained. Preparation of encapsulated phase change material with silica by spray drying would be experimentally investigated in the effect of the following parameters; on emulsion properties, thermal properties, encapsulation efficiency, morphology, the particle size distribution and material structure of the microencapsulated particles by using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), particle size analysis (laser light diffraction method), Fourier transform infrared spectroscopy (FT-IR) and N_2 sorption analysis using the following conditions;

3.1.1 The homogenizing speed which are 12,000, 14,000, 16,000 and 18,000 rpm

3.1.2 The homogenizing time which are 3, 5 and 7 minutes.

3.1.3 The content of the phase change material which is 20%, 33% and 50% weight of phase change material/ total solid weight.

3.1.4 The molar ratio of surfactant/phase change material (Tween20/PCM) which are 0.1:1, 0.5:1.

3.1.5 The condition of spray drying, the inlet temperature and the feed rate are 170 °C and 7.5 mL/min, respectively.

Expected benefits

1. To be able to prepare the microencapsulated phase change material that has the efficiency and sustainability.

2. To be able to reduce cost of the microencapsulated phase change material preparation.

3. To be able to use the instrument such as spray drying efficiently.

4. To obtain the knowledge about phase change material, sol-gel process, encapsulation and spray drying.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Phase change material.

Phase change materials (PCMs) are a substance that absorb, store, and release heat when they change state from liquid phase to solid phase or liquid to solid. Due to their property PCMs have received attention in many applications such as solar heating system, building energy conservation, air-conditioning systems and textile products. Many of phase change materials are available in any required temperature range. A classification of PCMs is given in Figure 2.1.

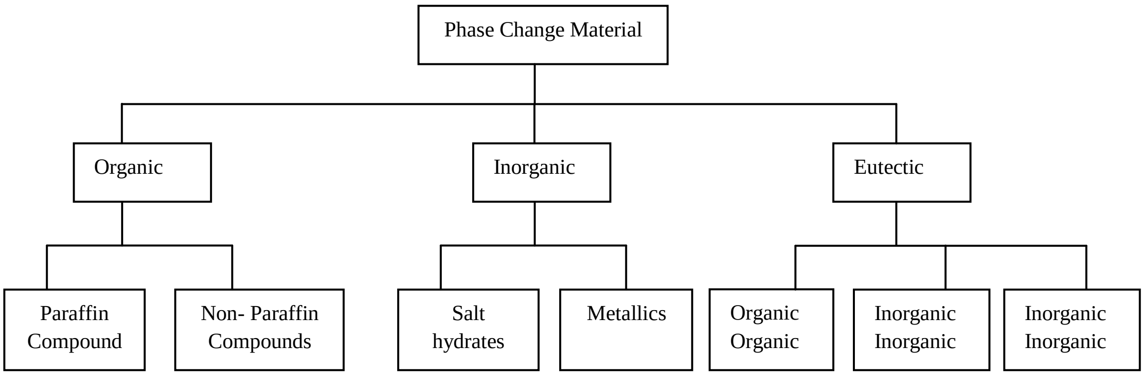


Figure 2. 1 Classifications of PCMs**.**

2.1.1 Organic phase change materials

2.1.1.1 Paraffins

Paraffin wax consists of a mixture of mostly straight chain *n*-alkanes CH_3–(CH_2)–CH_3. The crystallization of the (CH_3)- chain release a large amount of latent heat, the melting point and latent heat of fusion increase with chain length. Due to their availability in a large temperature range and their reasonably high heat of fusion, paraffins qualify as heat of fusion storage materials. Furthermore, they are known to freeze without supercooling.

2.1.1.2 Non-paraffins

These organic materials are further subgroups as fatty acids and other non-paraffin organic. Fatty acids are organic compounds characterized by $CH_3(CH_2)_{2n}COOH$. Moreover, Fatty acids are known to possess a reproducible melting and freezing behavior and freeze with little or no supercooling, they hence qualify as good PCMs.

2.1.2 Inorganic phase change materials

Inorganic materials are further classified as salt hydrates and metallics.

2.1.2.1 Salt hydrates.

Salt hydrates, characterized by $M.nH_20$, where M is an inorganic compound. The solid–liquid transformation of salt hydrates is actually a dehydration of hydration of the salt.

2.1.2.2 Metallics.

These metallics have not yet been seriously considered for PCM technology because of weight penalties. However, when volume is a consideration, they are likely candidates because of the high heat of fusion per unit volume.

2.1.3 Eutectic.

Eutectic is a minimum-melting composition of two or more components, each of which melts and freeze congruently forming a mixture of the component crystals during crystallization. Eutectic nearly always melts and freezes without segregation since they freeze to an intimate mixture of crystals, leaving little opportunity for the components to separate. On melting both components liquefy simultaneously, again with separation unlikely.

2.1.4 The advantages and disadvantage of phase change materials.

2.1.4.1 Organic phase change materials.

- Advantages.

1. Availability in a large temperature range.
2. Freeze without much super cooling.
3. Ability to melt congruently.

4. Self nucleating properties.
5. Compatibility with conventional material of construction.
6. No segregation.
7. Chemically stable.
8. High heat of fusion.
9. Safe and non-reactive.
10. Recyclable.

- Disadvantages.

1. Low thermal conductivity in their solid state. High heat transfer rates are required during the freezing cycle.
2. Volumetric latent heat storage capacity is low.
3. Flammable. This can be easily alleviated by a proper container.
4. Due to cost consideration only technical grade paraffin may be used which are essentially paraffin mixture and are completely refined of oil.

2.1.4.2 Inorganic phase change materials.

- Advantages.

1. High volumetric latent heat storage capacity.
2. Low cost and easy availability.
3. Sharp melting point.
4. High thermal conductivity.
5. High heat of fusion.
6. Low volume change.
7. Non-flammable.

- Disadvantages.

1. Change of volume is very high
2. Super cooling is major problem in solid-liquid transition.
3. Nucleating agents are needed and they often become imperative after repeated cycling.

2.1.4.3 Eutectic.

- Advantages.

1. Eutectics have sharp melting point similar to pure substance.
2. Volumetric storage density is slightly above organic compounds.

- Disadvantages.

1. Only limited data is available on thermo physical properties as the use of these materials are very new to thermal storage application [14].

Some of the important properties required for PCM are described as followed:

- High latent heat of fusion per unit mass, so that a lesser amount of material stores a given amount of energy.
- High specific heat that provides additional sensible heat storage effect and also avoid sub cooling.
- High thermal conductivity so that the temperature gradient required for charging the storage material is small.
- High density, so that a smaller container volume holds the material.
- A melting point in the desired operating temperature range.
- The phase change material should be non-poisonous, non-flammable and non-explosive.
- No chemical decomposition, so that the system life is assured.
- No corrosiveness to construction material
- PCM should exhibit little or no super cooling during freezing [15].

The thermophysical data for a range of typical and important PCMs studied or proposed for study by previous authors was showed as follow;

Table 2. 1 Thermophysical properties of PCMs investigated for different applications [16].

Compound	Melting temperature (°C)	Heat of fusion (J/g)
Water-ice	0	335
RT25–RT30	26.6	232
n-Octadecane	27.7	243.5
$CaCl_2.6H_2O$	29.9	187
$Na_2SO_4. 10H_2O$	32, 39	180
Paraffin wax	32–32.1	251
Capric acid	32	152.7
Polyethelene glycol 900 (PEG900)	34	150.5
Lauric–palmitic acid eutectic	35.2	166.3
Commercial paraffin wax	52.1	243.5
Palmitic acid	57.8–61.8	185.4
$Mg(NO_3)_2.6H_2O$	89	162.8
Erythritol	117.7	339.8

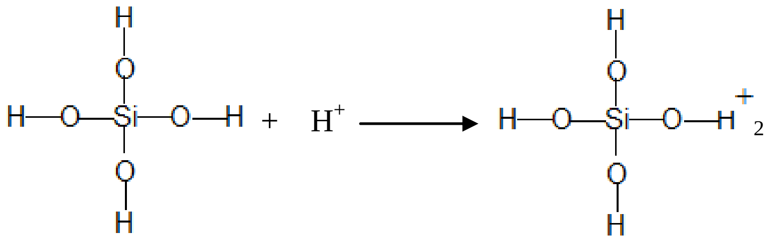
2.2 Sol-gel processing.

Sol gel process is a wet chemical technique widely used recently in the fields of material science and ceramic engineering. Firstly, the process starting from a colloidal solution (sol) that acts as the precursor for an integrated network (gel) containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions.

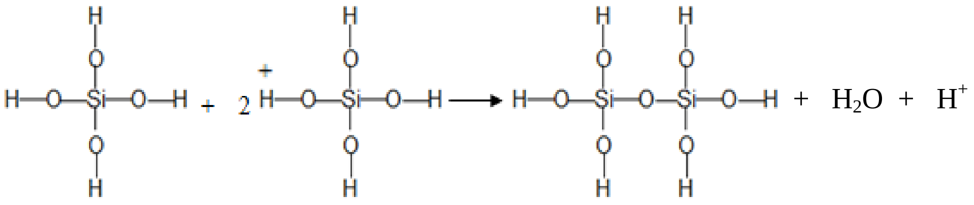
In addition, this system is used sodium silicate as a source of silica. Through this synthesis rout, the first step in the formation of silica is the release of $Si(OH)_4$ by hydrolysis of sodium silicate with hydrochloric acid according to the following equation:

$$Na_2SiO_3 + H_2O + 2HCl \longrightarrow Si(OH)_4 + 2NaCl \qquad \text{……….(1)}$$

Then, the $Si(OH)_4$ begins to polymerize with the removal of water this reaction occurs as follow:



$$\mathrm{H{-}O{-}Si(OH)_2{-}O{-}H} + H^+ \longrightarrow \mathrm{H{-}O{-}Si(OH)_2{-}O{-}H_2^+} \qquad \text{……….. (2)}$$



$$\mathrm{H{-}O{-}Si(OH)_2{-}O{-}H} + {}_2\overset{+}{}\mathrm{H{-}O{-}Si(OH)_2{-}O{-}H} \longrightarrow \mathrm{H{-}O{-}Si(OH)_2{-}O{-}Si(OH)_2{-}O{-}H} + H_2O + H^+ \qquad \text{……….. (3)}$$

The primary silica particles were formed as polymeric spheres by the polymer grow with the elimination of water. Moreover, to form silica gel, these primary particles commence to attach to each other through the silanol groups (SiOH) and the $Si(OH)_4$ rapidly condenses to SiO_2 with the removal of water, the reaction occurs as follow [17].:

$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O \qquad \text{……….. (4)}$$

2.3 Encapsulation.

Encapsulation is a process to trap one substance within another substance. The substance that is encapsulating may be called the coating, shell, wall material, external phase, or matrix. The substance that is encapsulated may be called the core material, the active agent, fill, internal phase. There are two main type of encapsulation might be distinguished that is the reservoir type and matrix type. The reservoir type has a shell around the core material, this type is also called capsule or single-core. Furthermore, the other type is the matrix type, the core material in the matrix type is much more dispersed over the shell material; it can be in the form of relatively small droplets or more homogenously distributed over the encapsulate. The core material in the matrix type of encapsulates are in general also present at the surface. For simplification, Figure 2.2 shows the spherical shaped encapsulates.

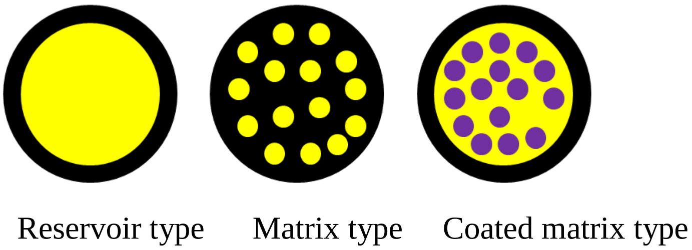


Figure 2.2 The spherical shaped encapsulates.

2.3.1 Advantages and disadvantages of encapsulation are described as followed:

Advantages

- Protect the substrate (core) from harmful environment and effect of oxygen
- Improved safety (e.g., reduced flammability of volatiles like aroma)
- Adjustable properties of active components (particle size, structure, oil or water soluble and color)
- Controlld release

Disadvantages

- Additional costs
- Stability challenges of encapsulates during processing and storage of the products

2.3.2 Encapsulation process can be distinguished as follow:

2.3.2.1 Mechanical process such as pan coating and spray drying

2.3.2.2 Physicochemical process such as simple and complex coacervation

2.3.2.3 Chemical process such as interfacial polymerization and in-situ polymerization

Many encapsulation processes are based on making first droplets of the active (in gas, liquid or powder form) and these droplets are subsequently surrounded by carrier material in a gas or liquid phase via different physico-chemical processes for example in Table 2.2 [18].

Table 2. 2 Common microencapsulation processes.

Technology	Process steps	Morphology	Load (%)	Particle size (µm)
Spray-drying	1. Disperse or dissolve active in aqueous coating solution 2. Atomize 3. Dehydrate	Matrix	5–50	10–400
Spray-chilling/ Cooling	1. Disperse or dissolve active in heated lipid solution 2. Atomize 3. Cool	Matrix	10–20	20–200
Emulsification	1. Dissolve active and emulsifiers in water or oil phase 2. Mix oil and water phases under shear	Matrix	1–100	0.2–5,000
Coacervation	1. Prepare o/w emulsions withlipophilic active in oil phase 2. Mix under turbulent conditions	Reservoir	40–90	10–800

Technology	Process steps	Morphology	Load (%)	Particle size (µm)
Coacervation	3. Induce three immiscible phases 4. Cool 5. Crosslink (optionally)			
Preparation of emulsions with multilayers	1. Prepare o/w emulsions with lipophilic active in oil phase and ionic emulsifiers 2. Mix with aqueous solution containing oppositely charged polyelectrolytes 3. Remove excess of free polyelectrolytes (option) 4. Repeat steps 2 and 3	Reservoir	1–90	0.2-5,000
Freeze- or vacuum drying	1. Dissolve or disperse active agent and carrier material in water. 2. Freeze the sample 3. Drying under low pressure 4. Grinding (option)	Matrix	Various	20–5,000

2.4 Spray drying

Spray drying is the method of producing a dry powder from a liquid or slurry by drying with a hot gas quickly, air is the heated drying media. Furthermore, if the liquid is a flammable solvent such as ethanol or the product is oxygen-sensitive then nitrogen is used. This drying method is wildly used for dry many thermally-sensitive materials such as foods and pharmaceuticals [19].

2.4.1 Principles of the Spray Drying Process.

Spray drying is described as the transformation of a feed from a solution, emulsion, dispersion, or paste into a dried particulate form by spraying the feed into a hot gaseous drying medium. It is a continuous one-step processing operation in which four different phases can be distinguished, namely:

- Atomization of the feed
- Mixing of spray and air
- Solvent evaporation
- Product separation

A variety of atomization systems are available, which may be classified according to the nozzle design as rotary atomization, pressure atomization, and two-fluid atomization.

2.4.1.1 In rotary atomization, the feed fluid is sprayed into the drying chamber by means of a spinning disc or wheel which creates a spray of droplets.

2.4.1.2 Pressure atomization occurs when the feed is fed to the nozzle under pressure which causes the fluid to be disrupted into droplets.

2.4.1.3 In two-fluid nozzles, the feed fluid and atomizing air are passed separately to the nozzle, where they mix, and the air causes the feed to break up into a spray.

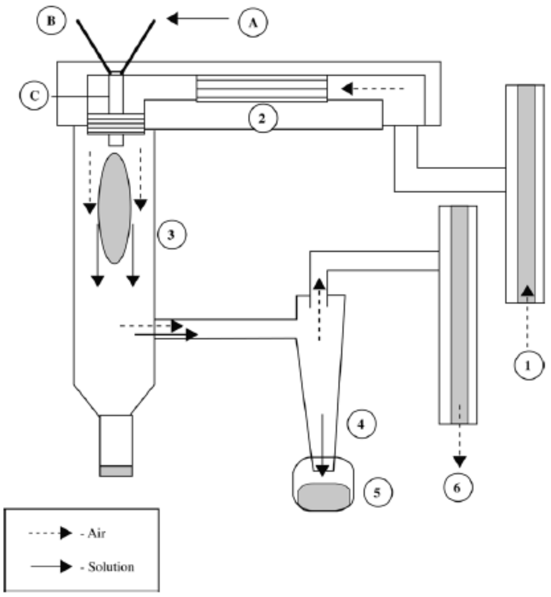


Figure 2. 3 Laboratory spray dryer: (1) drying air inlet and filtration; (2) heating; (3) desiccation chamber; (4) cyclone; (5) collector for drying powder-microspheres;(6) filtration and air outlet; (A) solution, suspension, emulsion to spray;(B) compressed or nitrogen air; and (C) spray nozzle (e.g., pneumatic, ultrasonic)

The particle size is depending on the selection of the atomizer. Rotating disks can be used with very viscous feeds, and thus allow for the formation of microspheres up to 200 mm. Two-fluid nozzle atomizers with nozzles of a typical internal diameter between 0.5 and 1.0 mm, lead usually to small microparticles with a diameter less than 10 mm.

Two different spray dryer designs can be distinguished. For the cocurrent manner operation, spray and drying air pass through the dryer in the same direction. Moreover, the counter-current operation is spray and drying air enters the drying chamber at opposite ends [20].

2.5 Microencapsulation of phase change materials.

Microencapsulation is the process of coating or surrounding one substance (core material) within another substance (shell material) on a very small scale [21]. PCMs have been used as a core material in the microcapsule production. There are many advantages of microencapsulated PCMs. For instance, increasing heat transfer area, reducing PCMs reactivity towards the outside environment and controlling the changes in the storage material volume as phase change occurs. Microcapsules are defined with the parameters such as particle diameter, thermal capacity and conductivity and PCM content of a capsule [22].

2.5.1 Classification of microencapsulation techniques [23].

There are two major classes of microencapsulation methods was describe as followed;

2.5.1.1 Chemical methods.

The chemical methods of microencapsulation involve polymerization during the process of preparing the microcapsules such as

- Interfacial polymerization.

This technique is characterized by wall formation via the rapid polymerization of monomers at the surface of the droplets or particles of dispersed core material. A multifunctional monomer is dissolved in the core material, and this solution is dispersed in an aqueous phase. A reactant to the monomer is added to the aqueous phase, and polymerization quickly ensues at the surfaces of the core droplets, forming the capsule walls. Cho et al. (2002) prepared the microcapsules containing octadecane as a phase change material for thermal adaptable application by interfacial polymerization in an emulsion system with toluene-2,4-diisocyanate (TDI) and diethylenetriamine (DETA) as a monomer and NP-10 was used as an emulsifier. The result showed that the polyurea microcapsule with diameter of about 1µm and the amount of latent heat was 112 J/g. The efficiency of octadecane encapsulation increased as the core content decreased [24]

- In situ polymerization.

In situ polymerization is a chemical encapsulation technique very similar to interfacial polymerization. The distinguishing characteristic of in situ polymerization is that no reactants are included in the core material. All polymerization occurs in the continuous phase, rather than on both sides of the interface between the continuous phase and the core material. Zhang et al. (2008) synthesized a microcapsule with a resorcinol-modified melamine–formaldehyde shell and *n*-octadecane core by in situ polymerization method using different emulsifiers and different surfactants in order to develop the fabrication of the modified melamine–formaldehyde shell of the microcapsules for better stability and to clarify the optimal conditions. The result showed that the resorcinol-modified melamine–formaldehyde shell was successfully fabricated on the surface of the core materials. Moreover, The microcapsules fabricated with a core/shell weight ratio of 75/25 have a compact surface of the shell and a mean particle size of below 20 µm and this condition is the optimal condition which has highest amount of latent heat was 146.5 J/g and a high efficiency of encapsulation about 92% [25]

- Coacervation.

Coacervation is a colloid phenomenon. If one starts with a solution of a colloid in an appropriate solvent, then according to the nature of the colloid, various changes can bring about a reduction of the solubility of the colloid. As a result of this reduction a large part of the colloid can be separated out into a new phase. The original one phase system becomes two phases. One is rich and the other is poor in colloid concentration. The colloid-rich phase in a dispersed state appears as amorphous liquid droplets called coacervate droplets. Upon standing these coalesce into one clear homogenous colloid-rich liquid layer, known as the coacervate layer which can be deposited so as to produce the wall material of the resultant capsules. Bay´es-Garcı´a et al. (2009) studied the preparation of phase change materials microcapsules by the coacervation method with different shell compositions, sterilized Gelatine/Arabic gum and Agar-Agar/Arabic gum. The aim of this study is to obtain microcapsules and the final procedures become the result of an optimization. The result showed that the microcapsules both have a spherical shape and their particle size distribution obtaining an average diameter of 12 µm for the sterilized Gelatine/Arabic gum microcapsules and lower values for the Agar-Agar/Arabic gum microcapsules. The amount of latent heat of the sterilized Gelatine/Arabic gum microcapsules and the Agar-Agar/Arabic gum microcapsules was 79, 78 J/g respectively [8]. Moreover, E. Onder et al. (2007) studied three types of paraffin waxes suitable for textile applications, namely *n*-hexadecane, *n*-octadecane and *n*-nonadecane encapsulated by complex coacervation of natural and biodegradable polymers, gum arabic–gelatin mixture, in order to investigate their heat storing or releasing capacities as well as their durability. FT-IR results have presented the proofs of successful complex coacervation of PCMs. One of the coacervates of *n*-hexadecane performed the enthalpy value of 144.7 J/g, while another coacervate containing *n*-octadecane provided 165.8 J/g and the coacervate including *n*-nonadecane presented enthalpy 57.5 J/g. For the studied coacervate percentages of fabrics, changing from 9.5% to 22.5%, the energy absorption capacities could be improved by 2.5–4.5 times relative to the references for particular temperature intervals [26].

- Emulsion polymerization.

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified with surfactants in a continuous phase of water. The name "emulsion polymerization" is a misnomer that arises from a historical misconception. Rather than occurring in emulsion droplets, polymerization takes place in the latex particles that form spontaneously in the first few minutes of the process. The particles are stopped from coagulating with each other because each particle is surrounded by the surfactant. Sar et al. (2009) prepared polymethylmetacrylate (PMMA) microcapsules containing n-octacosane as phase change material for thermal energy storage by emulsion polymerization. The result showed that the PMMA/octacosane microcapsules have spherical shape with a fairly uniform structure with diameter average 0.25 µm. The melting and freezing temperatures and the latent heats of the microencapsulated octacosane as PCM were measured as 50.6 and 53.2 ºC, 86.4 and-88.5 J/g, respectively by DSC analysis. TGA analysis indicated that the microencapsulated octacosane degrade in two steps and had good chemical stability [27].

- Sol-gel.

The sol-gel process starting from a colloidal solution (sol) that acts as the precursor for an integrated network (gel) containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions. The conditions of the process can be controlled by many factors including acid-base catalysis, surfactants, nature of silicon precursors, temperature, time, and mixing conditions. Zhang et al. (2009) investigated microencapsulated phase-change material (PCM) based on an n-Octadecane as core and an inorganic silica as shell through a sol–gel process. The result showed that the silica microcapsules synthesized at pH 2.45 displays a smooth and compact surface. These microcapsules also present a large particle size range of 7–16 µm. Thermogravimetric analysis showed that these silica microcapsules are degraded in two distinct steps, and have good thermal stability [6] and Chunyan et al. (2007) preparation of the phase change materials composites that composed of paraffin wax and silica in O/W emulsion and by sol-gel method, using Sodium silicate as a silica source to replace tetraethyl orthosilicate (TEOS) in order to reduce the cost of encapsulation PCM with silica. The result showed that the content of paraffin wax in the composite was 65wt%. The maximum latent heat and the average particle size of composite was 95 J/g and 5–6 µm respectively, and from using Sodium silicate as silica source, resulting in an amorphous silica [12]. Furthermore, Fang et al. (2010) synthesized microencapsulated paraffin composites with silica by sol-gel method, using shell as thermal energy storage materials tetraethoxysilane (TEOS) as a precursor. The result showed that the paraffin was successfully encapsulated in the shells of the silica, and the leakage of melted paraffin from the microcapsules can be prevented even when it was heated above the melting temperature of the paraffin. Furthermore, the size distribution of the microcapsules uniform and was about 8–15 µm, a latent heat of the microcapsules was 165.68 J/g [28].

-Suspension polymerization.

In suspension polymerization the initiator is soluble in the monomer, and these two are insoluble in the polymerization medium. The volume ratio of the monomer phase to the polymerization medium is usually kept within 0.1-0.5 but, in principle, it can be as high as unity or even higher. The monomer phase is, by means of a stirrer and a suitable droplet stabilizer (suspension agent), suspended in the medium in the form of small droplets (microdroplets). The polymerization is then initiated at the desired temperature is usually allowed to proceed to completion. Under these conditions, the monomer “microdroplets" are converted directly to the corresponding polymer “microbeads" of approximately the same size. Chang et al. (2009) studied the encapsulation of *n*-octadecane as phase change materials using a PMMA network-silica hybrid as the shell material based on the suspension polymerization method, using tetraethoxysilane (TEOS) as a silica source. The result showed that the microcapsules average size was about 10 µm, the highest amount of latent heat was 178.9 J/g and n-Octadecane content was 73.3% [29].

2.5.1.2 Physical methods

Physical methods of microencapsulation involves the controlled precipitation of a polymeric solution wherein physical changes usually occur such as Spray drying method, fluid bed coating method and centrifugal extrusion method, etc.

- Spray drying.

Spray drying is a mechanical microencapsulation method that an emulsion is prepared by dispersing the core material, usually an oil or active ingredient immiscible with water, into a concentrated solution of wall material until the desired size of oil droplets are attained. The resultant emulsion is atomized into a spray of droplets by pumping the slurry through a rotating disc into the heated compartment of a spray drier. There the water portion of the emulsion is evaporated, yielding dried capsules of variable shape containing scattered drops of core material.

The capsules are collected through continuous discharge from the spray drying chamber. This method can also be used to dry small microencapsulated materials from aqueous slurry that are produced by chemical methods. Hawlader et al. (2003) prepared microencapsulated paraffin particles for used as a solar-energy storage material by complex coacervation and spray drying method, and a comparison of the characteristic properties of the products was prepared. Gelatin and acacia in water were used as wall materials and the core materials was a paraffin wax. Microencapsulation by spray drying was carried out as emulsion of paraffin wax and the solutions of coating materials were spray-dried in the cocurrent mode using a Spray Dryer. The result showed that both complex coacervation and spray drying methods could be used to prepare microcapsules of paraffin wax. The microcapsules have a high energy storage and release capacities (145–240 J/g). Energy capacity depends on the core-to-coating ratio. Microencapsulation efficiency depends upon the process parameters, such as core-to-coating ratio, emulsifying time and the amount of cross-linking agent.SEM profiles show that the microcapsules are of spherical shape with a uniform size distribution. Coacervated and spray-dried microcapsules are suitable for a solar energy storage material [7] and Kortesuo et al. (2000) studied the evaluation of sol–gel processed spray dried silica gel microspheres as carrier in controlled drug delivery. The drug was dissolved in sol–gel processed silica sol before spray drying, silica sol was prepared by the hydrolysis and polycondensation of tetraethoxysilane (TEOS) with distilled water and acetic acid after that hydrolyzed silica sol was spray dried with a spray dryer which used inlet temperature 134°C,. The result showed spray drying is a promising way to produce spherical silica gel particles with a narrow particle size range for controlled delivery of drug [30]. Moreover, Kornbongkotmas (2011) investigated the preparation of spherical silica microcapsules containing Methyl palmitate as phase change material instead of n-Octadecane. The microcapsules were prepared in emulsion. The oil phase was PCM. The water phase is the silica sol-gel solution which was formed via sol-gel reaction of Tetraethyl orthosilicate (TEOS) with hydrochloric acid. Finally, the microcapsules were obtained by spray drying of an emulsion. The result showed that the microcapsules were spherical and nonporous, the average diameter was 10 µm, the amount of latent heat of the microcapsules that containing n-Octadecane and Methyl palmitate was 32.9 J/g, 29.4 J/g, respectively. %Encapsulation and %Retention of phase change materials in microcapsule were 14% and 70%, respectively [13].

2.6 Emulsions.

Emulsions are systems consisting of two or more immiscible liquid. For simple emulsions, the droplets of one liquid phase are dispersed in other immiscible liquid phase or continuous phase. To restrict the recombination of this two phase the emulsions system often consist a surfactant which to decrease the interfacial tension between phases and stabilize the dispersed-phase against coalescence once it is formed.

2.6.1 Classification of simple emulsions.

2.6.1.1 Water-in-oil (designated as W/O) emulsions.

The water-in-oil emulsions is a system which consists of the water droplets dispersed in an oil phase.

2.6.1.2 Oil-in-water (designated as O/W) emulsions.

The oil-in-water emulsions are a system consisting of oil droplets dispersed in an aqueous phase [31].

2.6.2 Surfactant

A surfactant is a substance that containing a hydrophilic head group (polar region), which has a high affinity for water, and a lipophilic tail group (non-polar region), which has a high affinity for oil.

2.6.2.1 Surfactant classification

Surfactants can be classified according to their physical properties or functionalities. The following is the most common classification and is based on the nature of the hydrophilic group.

Anionic: surface-active portion exhibits a negative charge

Cationic: surface-active portion exhibits a positive charge

Non-ionic: surface-active portion exhibits no charge

Zwitter-ionic: surface-active portion contains both negative and positive functional groups

2.6.2.2 Hydrophile-Lipophile Balance (HLB)

The HLB concept is a semi-empirical method that is widely used for classifying surfactants. The hydrophile-lipophile balance is described by a number that gives an indication of the relative affinity of a surfactant molecule for the oil and aqueous phases. Each surfactant is assigned a HLB number according to its chemical structure. A molecule with a high HLB number has a high ratio of hydrophilic groups to lipophilic groups, and vice versa. The HLB number of a surfactant can be calculated from knowledge of the number and type of hydrophilic and lipophilic groups it contains, or it can be estimated from experimental measurements of its cloud point. A widely used semi-empirical method of calculating the HLB number of a surfactant is as follows [32]

Table 2.3 HLB ranges and their general area of application.

Range	Application
3 – 10	Water-in-Oil emulsions (W/O)
7 –11	Wetting
11 – 18	Oil-in Water emulsions (O/W)
3 – 15	Detergency
15 – 18	Solubilisation

The emulsions are formed by solubilizing oil with a surfactant that has two main functions. First is decreasing the interfacial tension of the oil and water phase. Second is stabilizing the emulsion by preventing agglomeration, creaming, coalescence and breaking of the dispersed droplets. The performance of surfactant is depend on their characteristic such as critical micelle concentration (cmc).

Critical micelle concentration (cmc) is a concentration which the formation of surfactant aggregates occurs and the surface tension changes with a lower slope [33].

Table 2.4 Critical micelle concentration of some surfactant [34].

Surfactant	CMC(mM)	Molecular weight	Type
n-Decanoylsucrose	2.5	496.6	non-ionic
PLURONIC F-127	4-11	-	non-ionic
TRITON X-100	0.2-0.9	625	non-ionic
Tween 20	0.059	1228	non-ionic
CTAB	1.0	364.5	ionic
SDS	7-10	288.5	ionic
Cholic Acid, Sodium Salt	9-15	430.6	Ionic

CHAPTER III

RESEARCH METHODOLOGIES

3.1 Materials

Sodium silicate was purchased from Merck, Germany. Polyoxyethylene (20) sorbitan monolaurate or Tween 20 was purchased from Ajax Finechem, Australia. n-Octadecane with a purity of 99 wt.% was purchased from SAFC, United States and all chemicals used are the analytical grade.

3.2 Preparation of encapsulated phase change materials

3.2.1 Preparation of emulsion.

The emulsion was obtained by Tween 20 as an emulsifier was dissolved in demonized water. n-Octadecane was added into the Tween 20 solution. Sodium silicate solution (SiO_2 27 wt%, Na_2O 8 wt %) was diluted with 30 ml deionized water. Then, HCl was added into the sodium silicate solution. During the stirring, Tween 20 solution was added into sodium silicate solution. The mixture was homogenized by a homogenizer (Model T-25D Ultra-Turrax, IKA, German) at 12,000, 14,000, 16,000 and 18,000 rpm for 3, 5 and 7 minutes. The emulsion was aged at 35 °C for 3 hours before spray dried due to the stickiness of powders and Tween 20 which is a viscous liquid surfactant on the chamber and cyclone walls during drying. After aged the emulsion for 3 hours the microcapsule was successfully prepared by spray drying because of the gelation occur, surfactant and n-Octadecane were trapped inside of the silica gel network.

3.2.2 Preparation of microcapsules by spray drying.

Spray drying of feed emulsion was carried out in B-290 (Büchi Labortechik AG, Switzerland). The operation conditions of the spray drying were as follows: inlet air temperature: 170 ºC, outlet air temperature: 110-120 ºC, feed flow rate: 7.5 mL/min, air flow rate: 6,183 mL/min. The typical synthetic procedure is carried out as follows:

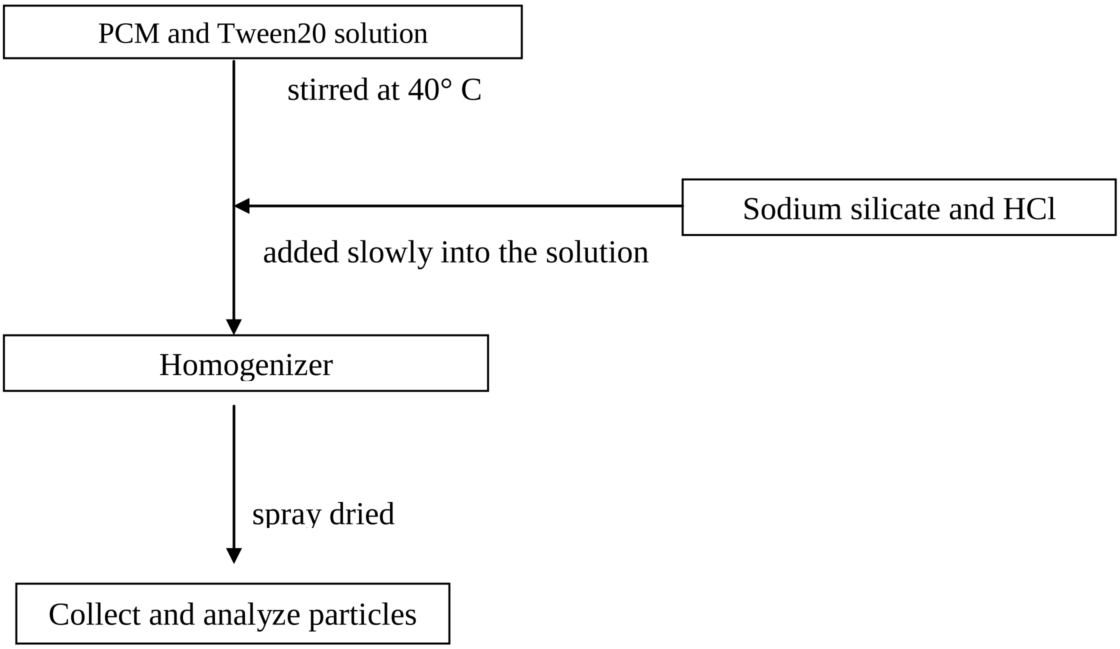


Figure 3. 1 Preparing the encapsulate phase change material.

3.3 Analysis of emulsions

The characteristics of O/W emulsion which the oil phase is n-Octadecane and water phase is the silica sol-gel solution were observed by using various techniques including:

3.3.1 The dispersion of oil droplets

The dispersion of oil droplets throughout a water phase was investigated by Light microscope (Olympus, 40x). A drop of emulsion sample was placed on a glass slide and covered with a cover slip. Then, the sample was examined and an image was captured.

3.3.2 The emulsion droplets size and size distribution

- The droplets size and droplets size distribution were determined on a particle size analyzer (HORIBA, LA-950) by using refractive index of n-Octadecane which is 1.4390±0.01i. The sample was diluted in the water before the measurements were started.

3.4 Analysis of microcapsules

In order to removing PCMs at the surface of microcapsules, the 1 g of microcapsules was washed 5 times with Hexane 2 mL after spray drying. Finally, the characteristics and performance of microcapsule were investigated by various techniques as described as follows:

3.4.1 Microstructure of microcapsules

In this research the shape of microcapsules, the outer surface and the inner surface of microcapsules were observed by using a scanning electron microscope, SEM (JSM-6400, JEOL Co., Ltd.). The sample microcapsules were stuck on stub with black two sided tape and coated with gold film and then examined by SEM and taken a photo.

3.4.2 Energy storage and release capacities

The energy storage and release from microencapsulate phase change material were determined by a Differential scanning calorimeter (Mettler Toledo, 823e). These measurements, a sample weight around 5-8 mg were placed in a Aluminum sample pan. The sample was heated varying the temperature in the range from −10 to 100 °C with a heating rate of 10 °C/min.

3.4.3 Chemical structure evaluation

The chemical structure of microcapsules was evaluated by Fourier transforms infrared spectroscopy (FT-IR) to analyze the functional group. Fourier transform infrared (FTIR) spectra of the samples were obtained using a Fourier Transform Infrared Spectrometer (PerkinElmer, Spectrum One). The samples were pressed to form pellets by mixing with pure and dry crystalline KBr (Sample:KBr = 1:100) for FT-IR instrumental analyses. Measurements in the range of medium IR 4000-400 cm^{-1}, number of scans 16 and resolution 4 cm^{-1} characterized these measurements.

3.4.3 The particle size and Particle size distribution

The particle size and Particle size distribution were determined on a particle size analyzer (HORIBA, LA-950) by using refractive index of Silica which is 1.455±0.01i. The microcapsules sample was diluted in the isopropanol before the measurements were started.

CHAPTER IV

RESULTS AND DISCUSSION

The phase change materials can be applied to absorb and release heat in many uses. In this study, the problem when using phase change materials has been solved. The microcapsules which contain n-Octadecane were prepared via sol gel and spray drying process. The properties of microcapsule were investigated by many techniques.

4.1 The chemical structure of the shell material.

4.1.1 Fourier transform infrared spectroscopy (FTIR) study.

The shell material which prepared from adding hydrochloric acid into sodium silicate solution and aged for 3 hours. After that, the mixture was spray dried at the operating conditions used are as follows: inlet air temperature was 170 ^{o}C, outlet air temperature was 110-120 °C, feed flow rate: 7.5 ml/min, air flow rate: 6,183 ml/min.

The chemical structure of the shell material was investigated by using Fourier Transform Infrared Spectroscopy. Figure 4.1 shows the spectra of the silica shell that prepared from sodium silicate. The intensity of the bonds at 3500 and 1600cm^{-1} which related to O-H groups [35]. The peaks were detected around 460, 800 and 1070 cm^{-1} are attributed to O−Si−O rocking vibration band, Si−O bending vibration band and Si−O−Si antisymmetric stretching vibration band respectively which are the main characteristic peaks of Si−O−Si bonds vibrational modes[17].

Zhang et al.[6] were also reported the quite similar peaks at 1084 and 461 cm^{-1} that are attributed to asymmetric and symmetric Si–O–Si stretching vibrations of the silica shells respectively.

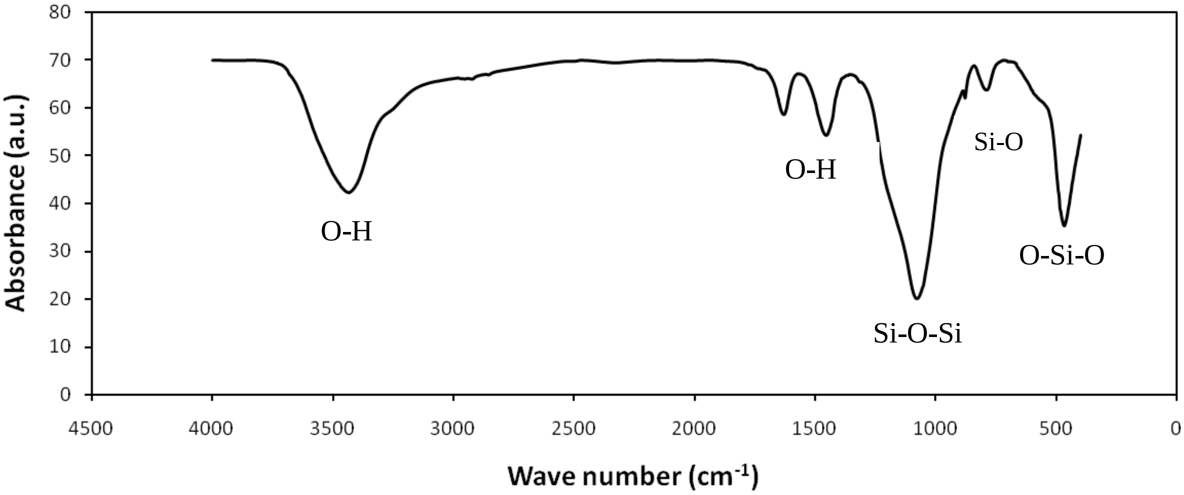


Figure 4.1 FTIR spectra of the silica shell.

4.1.2 The elemental analysis of microcapsules shell.

In this study silica shell was prepared via sol gel process of sodium silicate solution by adding hydrochloric acid according to the following equation and spray drying sol gel solution to form silica shell powder without removing the sodium chloride.

$$Na_2SiO_3 + H_2O + 2HCl \longrightarrow Si(OH)_4 + 2NaCl$$

The elemental analysis of the shell material was obtained by using Energy-dispersive X-ray spectroscopy. Figure 4.2 shows the elements present that the element C is 12.38%, O is 49.51%, Na is 11.59%, Si is 26.21% and Cl is 0.32% respectively. The silica shell had the presence of sodium, this implied that during reaction the sodium chloride was trapped inside the gel network and there are Na_2SiO_3 which was not react to form $Si(OH)_4$. For the removal Na+, an ion exchange method can be performed but is expensive, take long time and worthwhile only for special applications such as biological applications.

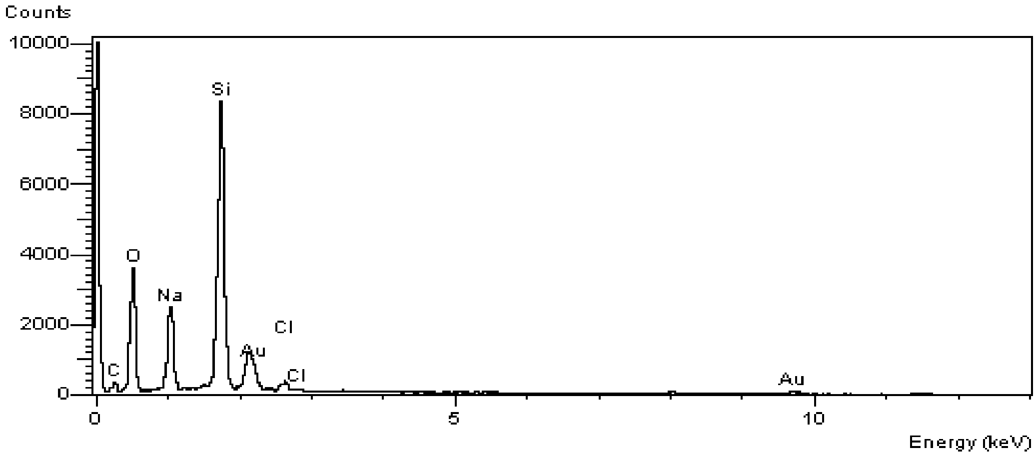


Figure 4.2 SEM-EDX Analysis Result of the microcapsules shell.

4.1.3 The morphology of silica shell powder.

Figure 4.3 shows SEM images of silica powder produced by spray drying method from sodium silicate solution prepared by adding hydrochloric acid. It can be observed that the morphology of the silica particles produced is hollow spherical particles and doughnut-shaped particles that are the model of spray-dried products.

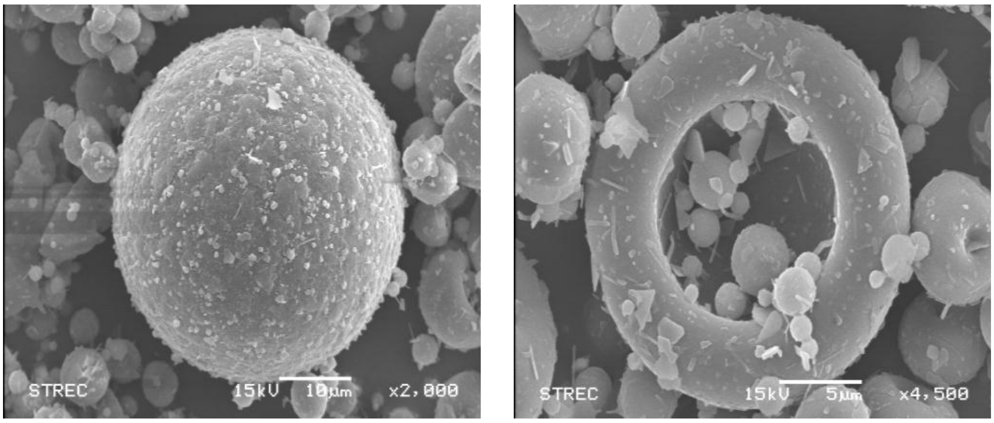


Figure 4. 3 The SEM micrograph of silica shell powder which prepared by reacting sodium silicate with hydrochloric and aged for 3 hours before spray-dried.

There are various product forms which can prepared from spray drying process such as porous particle, hollow particle, doughnut particle, raspberry particle and hairy particle. The morphology of the product from spray drying is depended on the properties of raw material and process conditions.

In this research, the morphology of microcapsule was observed as the two types which are hollow spherical shape and doughnut shape. The formation mechanism of hollow spherical and doughnut-shaped particles was showed in the figure below. Due to the evaporation of the emulsion droplet, the water at the surface starts to evaporate that leads to increasing the sodium silicate concentration at the surface so the silica layer was form. Moreover, when the evaporation occur the water within droplet diffuse to the surface and the expansion of hot air within the droplet result in a center void of particles.

A doughnut shape was formed by the change of a droplet from spherical shape to a mushroom and convex shape during the spray drying process. The mass and the heat transfer of the droplet can result in the formation of doughnut particles as showed in figure

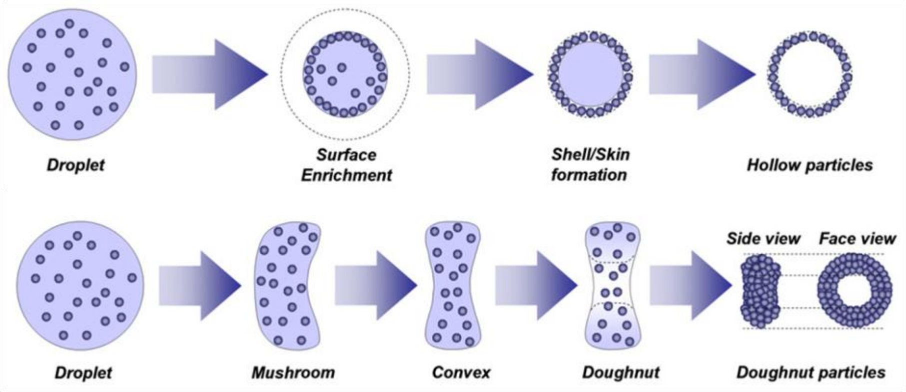


Figure 4.4 Formation mechanism of hollow spherical and doughnut-shaped particles [36].

4.2 Effect of the homogenizing speed.

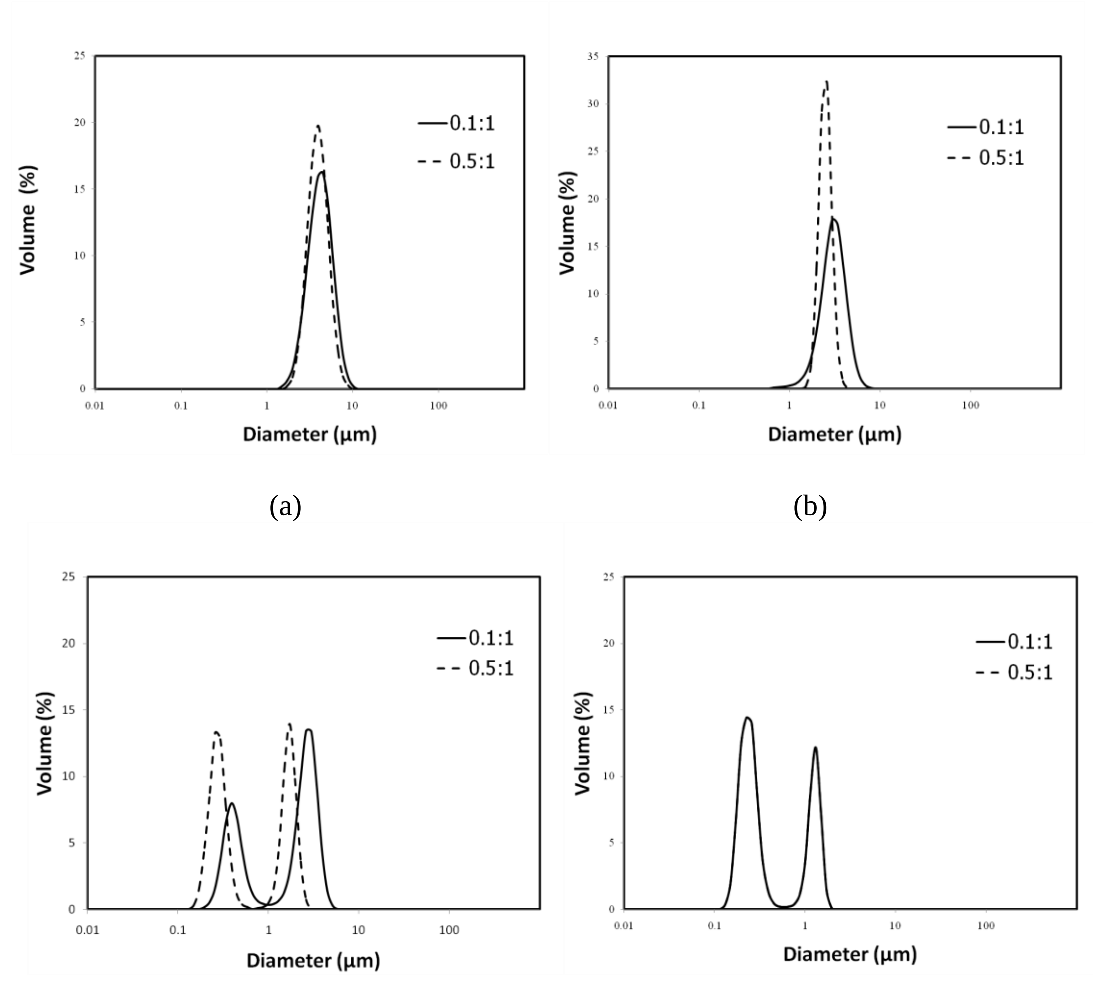
4.2.1 Effect of the homogenizing speed on emulsion droplet size.

The objective of this study is to find the conditions which emulsion droplets size is small, a small size is important for high PCMs content in the microcapsule. The homogenizing speed and homogenizing time in the preparation of emulsion are the parameter that the droplet size is depending on. In this research the O/W emulsion was prepared by adding the mixture of n-Octadecane and the Tween 20 solution into Sodium silicate solution. The mixture was homogenized by a homogenizer. The O/W emulsion was investigated by Light microscope and Particle size analyzer.

In this research, the results show that the homogenizing speed influences the mean droplets size of emulsion as show in Figure 4.4, For increasing homogenizing speed from 12,000 rpm to 18,000 rpm, the mean droplets size diameter decrease from 4.07 to 2.93, 1.77 and 0.57 µm for the Tween 20: PCMs molar ratio 0.1:1 and 3.75 µm to 2.35, 0.87 and 0.56 µm for the Tween 20: PCMs molar ratio 0.5:1. In this study the emulsion was prepared from the homogenization that reduces the interfacial tension of the oil and water phases by the shear. The shear is the operation of homogenization that separates a dispersed phase droplet because of different fluid velocities surrounding the droplet. This implies that the high shear rate bring the smaller droplets formation in emulsion.

Figure 4.5 (a) to 4.5 (d) show the distribution curve of the emulsion droplet size of the emulsion which prepared at the molar ratio of Tween 20: PCMs are 0.1:1 and 0.5:1, homogenizing speed of 12,000, 14,000, 16,000 and 18,000 rpm respectively. First of all, for the Figure 4.5 (a) and 4.5 (b) the emulsion prepared at 12,000 and 14,000 rpm respectively show the unimodal distribution (normal distribution). However, for the higher homogenizing speed which are 16,000 and 18,000 rpm the emulsion droplets size distribution is the bimodal that show in the figure 4.5 (c) and 4.5 (d) respectively. For Figure 4.5 (d) the two lines are overlay.

This is the result of the high homogenizing speed cause the high shear force that make the small emulsion droplets. The small emulsion droplets contribute to agglomerate with another droplet beside them which leads to complete phase separation because of the contact between water and oil molecules is energetically unfavorable, so that the emulsions of this conditions (the molar ratio of surfactant: the oil phase is 0.1:1 and 0.5:1) are thermodynamically unstable systems. Thermodynamically unstable system is the system that containing two or more immiscible phases, involve thermodynamic conditions in which the primary driving force is to reduce the total interfacial area between the phases, emulsions will tend to reduce their total free energy through an increase in droplet size[33].



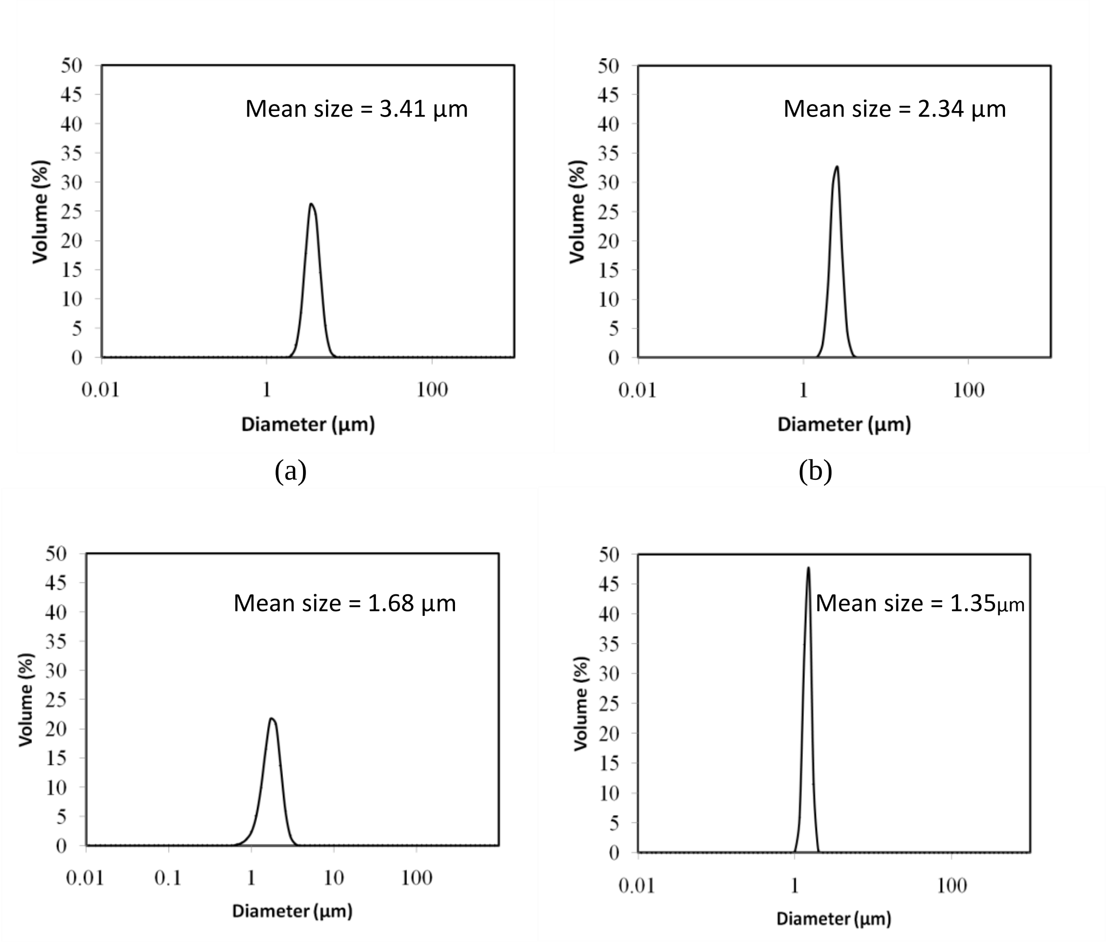
(a) (b)

(c) (d)

Figure 4.5 The effect of homogenizing speed on the droplet size distribution of the emulsion which prepared at the content of the phase change material which is 20%, the Tween 20: PCMs molar ratio (——) 0.1:1 and (-----) 0.5:1 and the homogenizing speed is (a) 12,000, (b) 14,000, (c) 16,000 and (d) 18,000 rpm**.**

Moreover, the emulsion droplets size distribution of the sample which prepared at the molar ratio of Tween 20: PCMs is 0.5:1 are essentially similar with the ratio 0.1:1 but at the molar ratio of Tween 20: PCMs is 0.5:1 shows more narrow droplets size distribution because the high content of surfactant which leads to more stable system that can prevents the droplets from agglomeration to be a larger droplet.

The kinetically stable that is due to the presence of an adsorbed layer at the o/w interface. These barriers not only prevent emulsion droplets from coming into the direct contact, but also serve to stabilize the thin film of liquid between two adjacent droplets of interaction between large monomer droplets is very low, and most interactions. For preparing the kinetically stable emulsion [37], the emulsifiers or surfactants were needed because the surfactant is a surface-active molecule that adsorbs to the surface of freshly formed droplets during homogenization, forming a protective membrane that preventing agglomeration of the droplets that coming close enough. This suggests that the surfactant enhance emulsion stability by interrupting the movement of the droplets [31]. In this research we found that the optimum content of surfactant which is a stable system for homogenizing speed 12,000 to 18,000 rpm is 1.6:1 as showed in Figure 4.6. Even though the optimum condition for preparing emulsion is at the molar ratio of Tween 20: PCMs is 1.6:1, but the emulsion of this condition is unsuitable for preparing microcapsules by spray drying because of Tween 20 property that is a viscous liquid surfactant. After the emulsion contact with the hot air the many microcapsules were stuck in the drying chamber and cyclone during spray drying process and no microcapsule in the collector.



(a) (b)

(c) (d)

Figure 4.6 Effect of the homogenizing speed on the emulsion droplet size distribution using the mole ratio of Tween 20 : PCMs which is 1.6:1, The content of the phase change material which is 20%. and the homogenizing speed is (a) 12,000, (b) 14,000, (c) 16,000 and (d) 18,000 rpm.

Figure 4.7 shows the effect of the homogenizing speed on the emulsion droplet size distribution which prepared in homogenizing speed of 12,000, 14,000, 16,000, 18,000 rpm at the molar ratio of Tween 20: PCMs is 0.1:1 and 0.5:1, the droplet size distribution is a normal distribution for homogenizing speed 12,000 rpm and 14,000 rpm and bimodal distribution for homogenizing speed 16,000 rpm and 18,000 rpm as describe in 4.2.1 and the result of a high shear rate caused the formation of smaller droplets in the emulsion as showed in Figure 4.7.

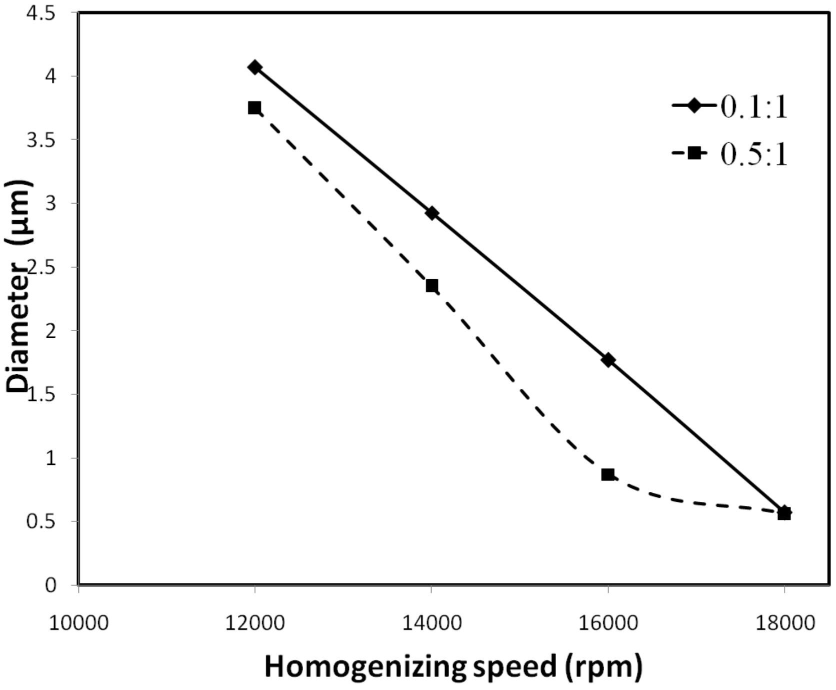
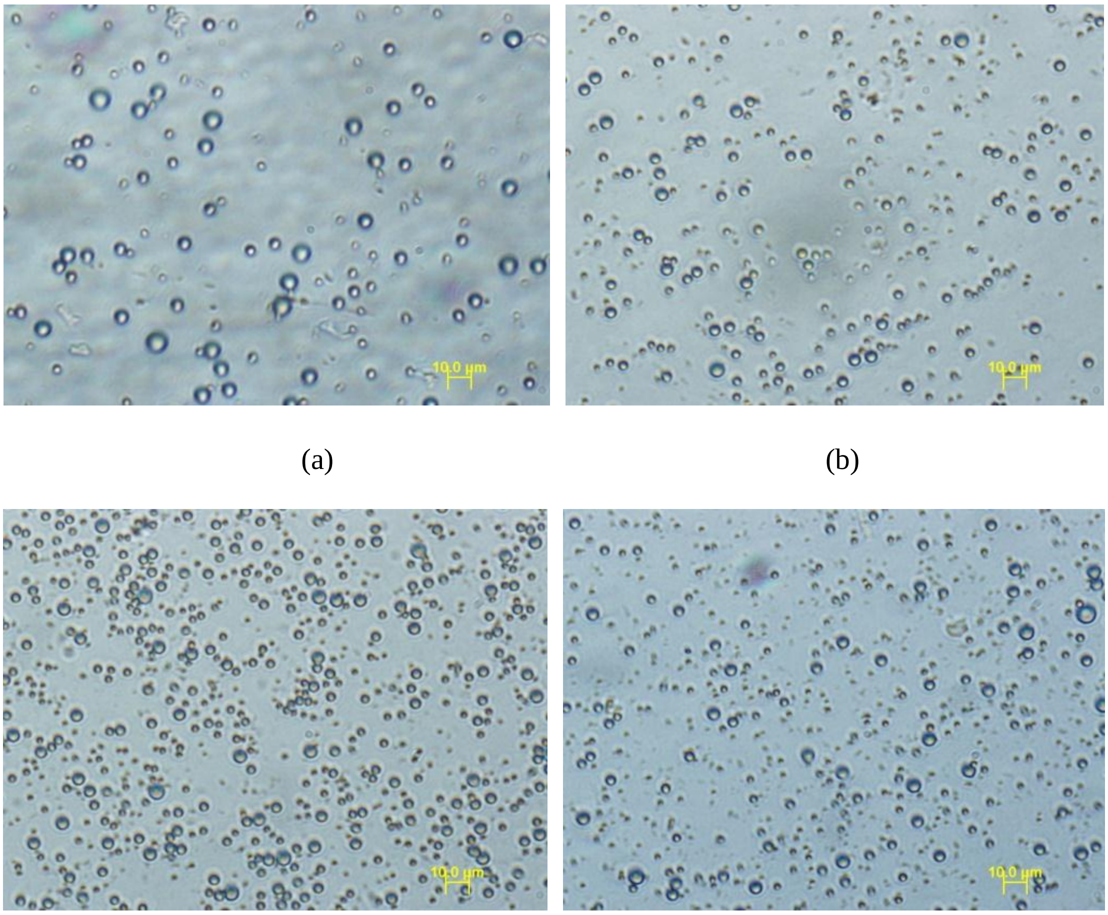


Figure 4.7 Effect of the homogenizing speed on the emulsion droplet size diameter using the mole ratio of Tween 20 : PCMs which is (——) 0.1:1 and (----) 0.5:1, The content of the phase change material which is 20%.

A micrograph of O/W emulsion which contain n-Octadecane as the oil phase and silica sol gel solution as the water phase was showed in Figure 4.7.

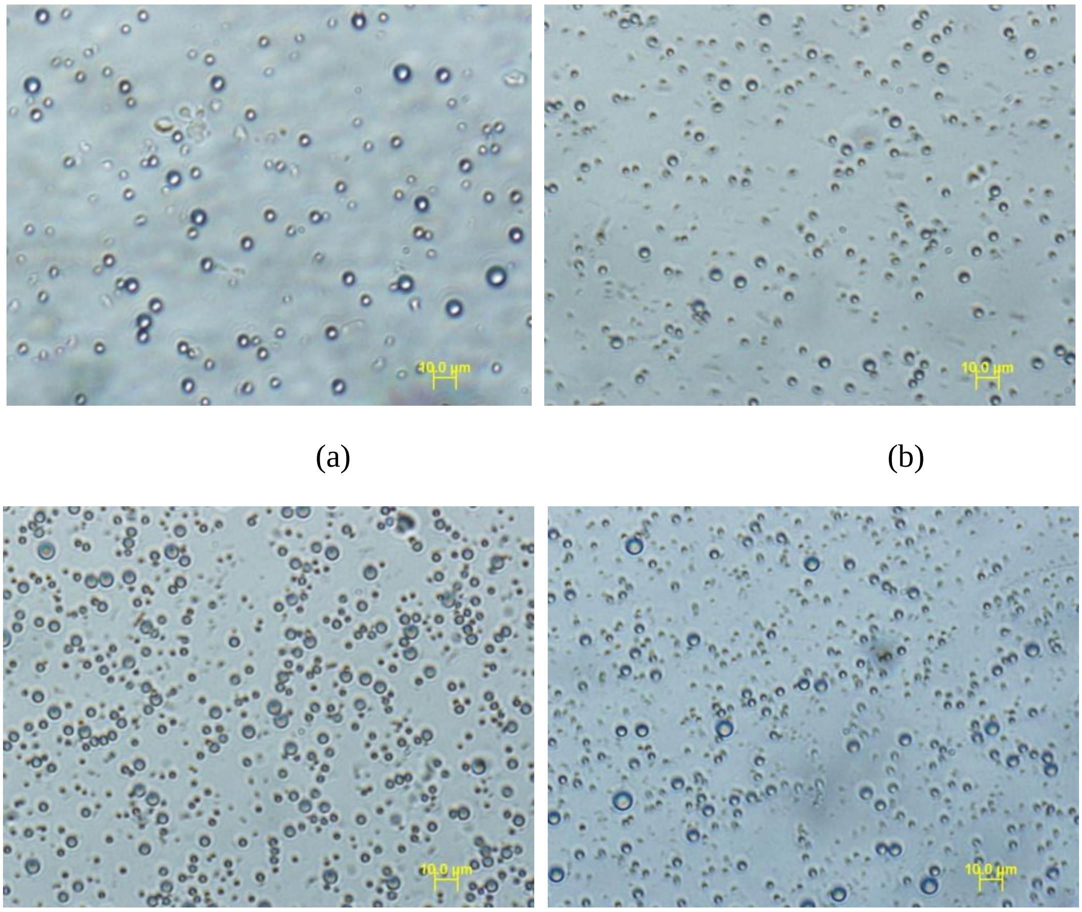
Figute 4.8 and 4.9 show a light microscope image of O/W emulsion which prepared for different homogenizing speed at the mole ratio of Tween 20: PCMs which is 0.1:1 and 0.5:1 respectively. The micrographs show many small PCM droplets of n-Octadecane were suspended as the dispersed phase throughout the continuous phase which is silica sol-gel solution, the two phases immiscible with each other. In addition, the droplets look smaller with higher homogenizing speed due to the shear rate is increased. Moreover, Figure 4.8 (c), 4.9 (c) and 4.8 (d), 4.9 (d) represent the image of O/W emulsion which prepared at homogenizing speed 16,000 rpm and 18,000 rpm respectively show there are different size of the droplets in picture that correspond to the bimodal droplets size distribution result as show in Figure 4.5. This result is similar with emulsion that prepared at the mole ratio of Tween 20: PCMs which is 0.5:1.



(a) (b)

(c) (d)

Figure 4.8 The micrograph of the emulsion using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is 20% and the homogenizing speed is (a) 12,000, (b) 14,000, (c) 16,000 and (d) 18,000 rpm.



(a) (b)

(c) (d)

Figure 4.9 The micrograph of the emulsion using the mole ratio of Tween 20: PCMs which is 0.5:1, the content of the phase change material which is 20% and the homogenizing speed is (a) 12,000, (b) 14,000, (c) 16,000 and (d) 18,000 rpm.

4.2.2 Effect of the homogenizing speed on the morphology of microcapsule.

Surface and inner structure of microcapsules obtain from spray drying process were investigated by using a scanning electron microscope (SEM). The microcapsules were put into Hexane for removing PCM at the surface. Figures 4.10 shows SEM micrographs of microcapsules containing PCMs. The inner microstructures of the microcapsules which prepared at the different homogenizing speed. The image shows the regular spheres shape and most of the microcapsules have smooth surfaces. Unfortunatly, there are some dimples were found on some of the microcapsules. The inner structure of microcapsules which prepared from spray drying show the coating material form the capsule wall and the inner structure is a matrix type. Moreover, the core PCM was found as discrete particles embedded in the inner matrix of wall of capsule and due to the spray drying method, there are some holes were found the inner structure because of evaporation of water during drying [38].

4.2.3 Effect of the homogenizing speed on the retention of n-Octadecane.

The n-Octadecane retention was described as the ratio of the n-Octadecane in the powder to the n-Octadecane in the feed emulsion. The microcapsules were put into Hexane for removing PCMs at the outer surface before evaluated the enthalpies by DSC, the result of the samples before washing and after washing were used for determine the retention of microcapsule.

Figure 4.11 shows the effect of the homogenizing speed on %Total retention. For the n-Octadecane loading 33 wt% and 50 wt%, the Total retention increase with increasing homogenizing speed due to the small emulsion droplets size. This suggests that the emulsion droplet size is a important factor for the retention of n-Octadecane, this result agree with A. Soottitantawat et al [39] who represented the increasing retention of d-limonene with decreasing emulsion diameter due to the fact that a fine emulsion is stable during both the atomization and spray drying. Nevertheless, for the n-Octadecane loading 20% the increasing homogenizing speed resulted in a decreasing retention because for the low content of n-Octadecane in emulsion. In this study the %Solid content in emulsion feed not change for all sample so the H_2O/Si molar raio (R) of sample which contain 20 wt% of n- Octadecane is lower than the H_2O/Si molar raio of sample which contain 33 wt% and 50 wt% of n-Octadecane. Klein et al [40] represented higher values of R, the silicate concentration is reduced. This in turn reduces the hydrolysis and condensation rates, resulting in longer gelation times. It’s implied that at 20 wt% of n-Octadecane in emulsion feed the gelation occurs faster than 33 wt% and 50 wt% and so result in high viscosity of emulsion feed. In addition, the sample 20 wt% also show the retention decreases with the homogenizing speed increases because of increasing homogenizing speed to 16,000 and 18,000 rpm resulted in temperature of feed increases that lead to increasing of rate of hydrolysis and polycondensation that result in high viscosity of emulsion feed. Moreover, the increase on feed viscosity can cause more solids to paste in the main chamber wall, thus reducing the retention [41].

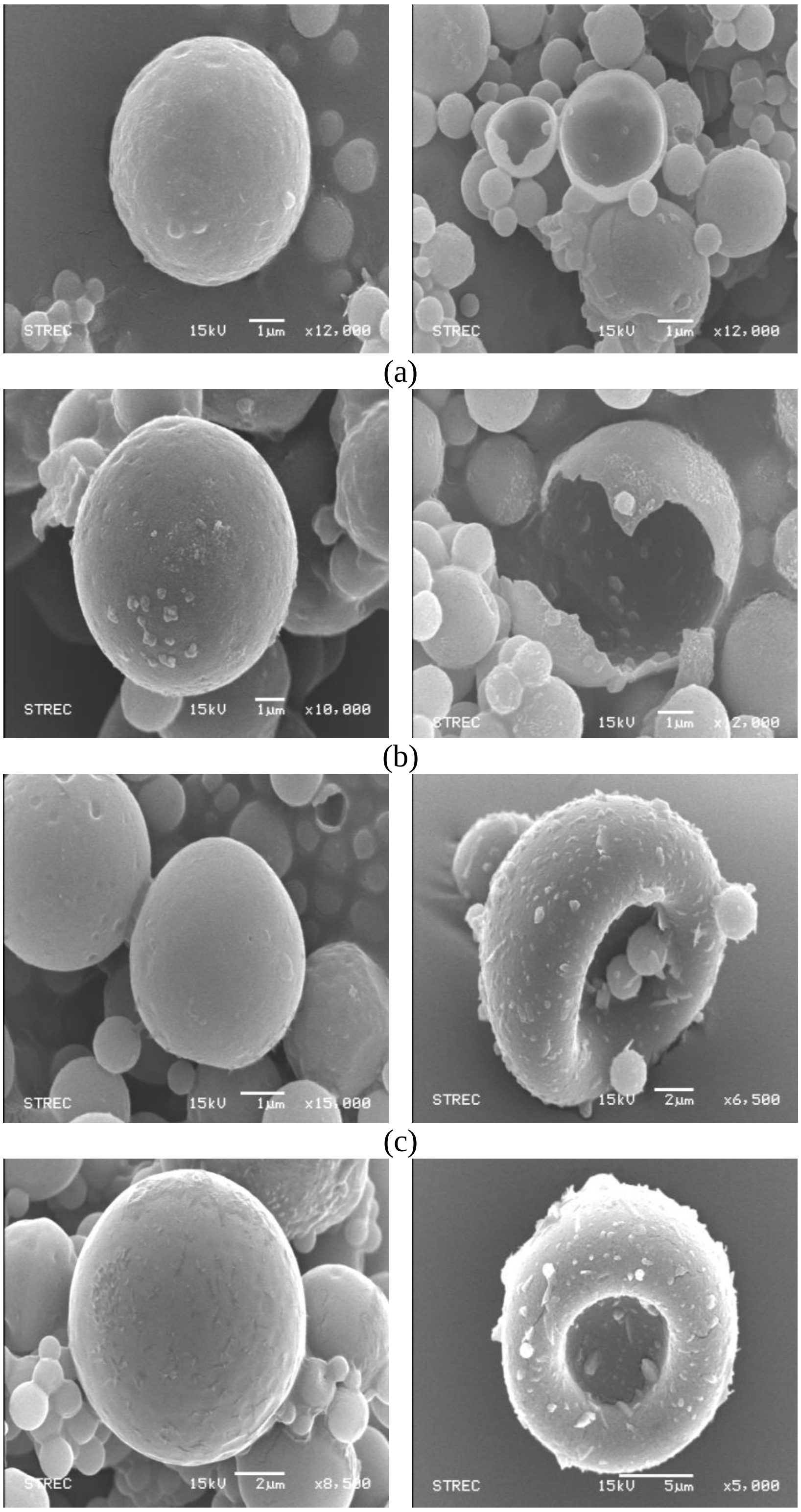
Figure 4.12 shows the effect of the homogenizing speed on %Retention in . For the n-Octadecane loading 33 wt% and 50 wt%, the %Retention in increase with increasing homogenizing speed due to the small emulsion droplets size. This suggests that the smaller n-Octadecane droplets lead to good embed throughout the microcapsule. However, for the n-Octadecane loading 20 wt%, the %Retention in decrease with increasing homogenizing speed because the high rate of hydrolysis and condensation reaction of this condition, this implied that for the same aging time, the emulsion which contain n-Octadecane 20 wt% took long gelation time. As a result, there are a few n-Octadecane embedded in microcapsules. This result agree with S.Kornbongkodmas [13] who represented long gelation time causing the low %Retention in of microcapsule because the long gelation time leads to the high thickness of the silica shell. The microcapsules were cracked by the expansion of hot air within the droplet during spray drying process so resulted in a few n-Octadecane content in the microcapsule.

The %Retention out of n-Octadecane was showed in Figure 4.13. The %Retention out of the sample of 20% and 33% n-Octadecane loading are the same with increasing homogenizing speed but for the sample of 50% n-Octadecane loading the %Retention out increases with increasing homogenizing because of the too high n-Octadecane content is excessive for encapsulation.

4.2.4 Effect of the homogenizing speed on the of n-Octadecane content in microcapsule.

The %Content of n-Octadecane was described as the weight ratio of the n-Octadecane in the powder to the total solid.

Figure 4.14 and Figure 4.15 shows the effect of the homogenizing speed on %Content and %Encapsulation respectively. For the n-Octadecane loading 33 wt% and 50 wt%, the %Content and %Encapsulation increase with increasing homogenizing speed due to the small emulsion droplets size. These results suggest that a smaller emulsion droplets size leads to a high %Content of n-Octadecane. In addition, for the sample which prepared at the 20% and 33% 0f n-Octadecane loading shows a smaller amount of surface oil than the surface oil of 50% n-Octadecane loading as showed in Figure 4.16 due to the too much amount of n-Octadecane.



(a)

(b)

(c)

(d)

Figure 4.10 The SEM micrograph of silica microcapsules which synthesized at the mole ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 20% and the homogenizing speed is (a) 12,000, (b) 14,000, (c) 16,000 and (d) 18,000 rpm.

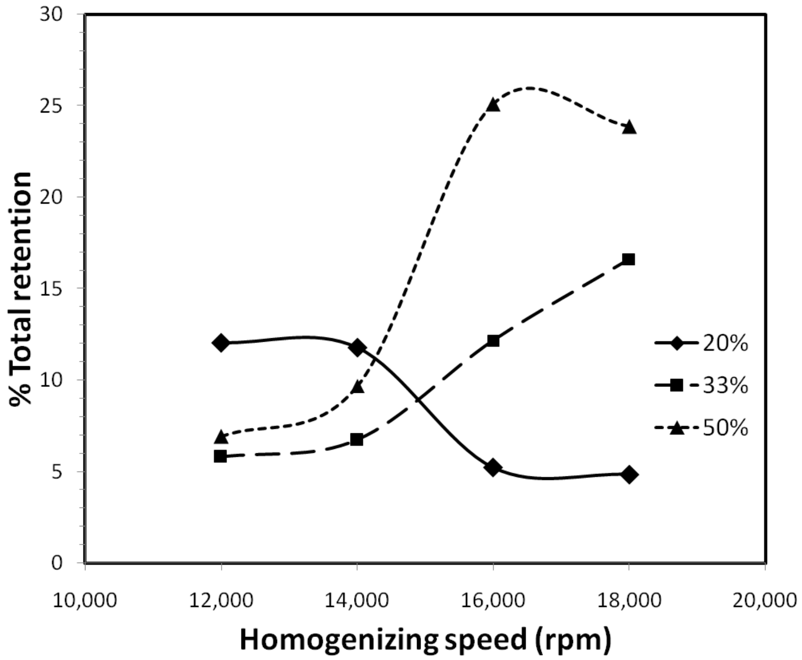


Figure 4.11 The effect of the homogenizing speed on %Total retention of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is (a) 20%, (b) 33% and (c) 50%.

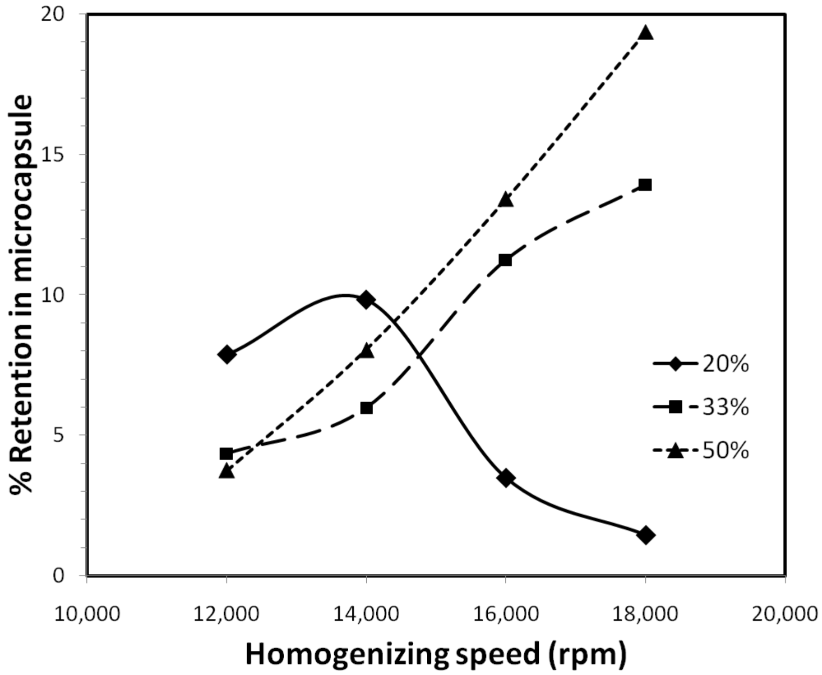


Figure 4.12 The effect of the homogenizing speed on %Retention in of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is (a) 20%, (b) 33% and (c) 50%.

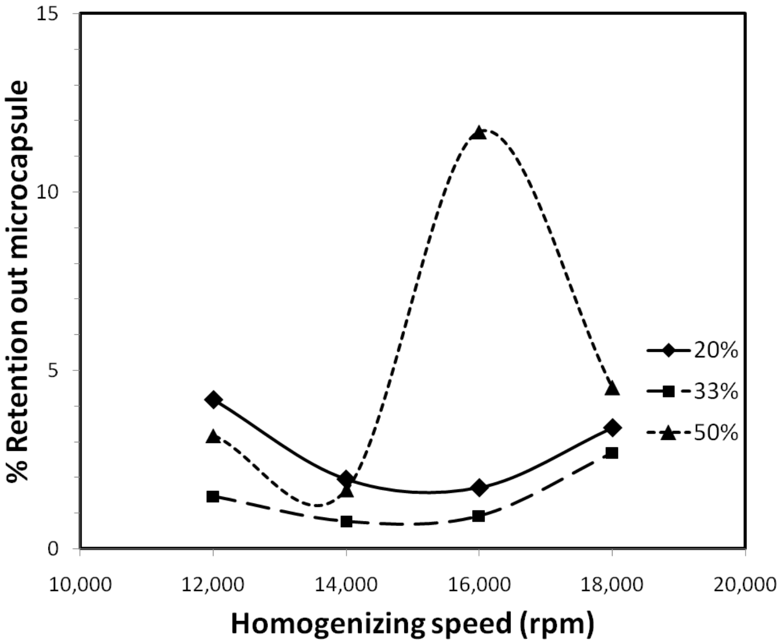


Figure 4.13 The effect of the homogenizing speed on %Retention out of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is (a) 20%, (b) 33% and (c) 50%

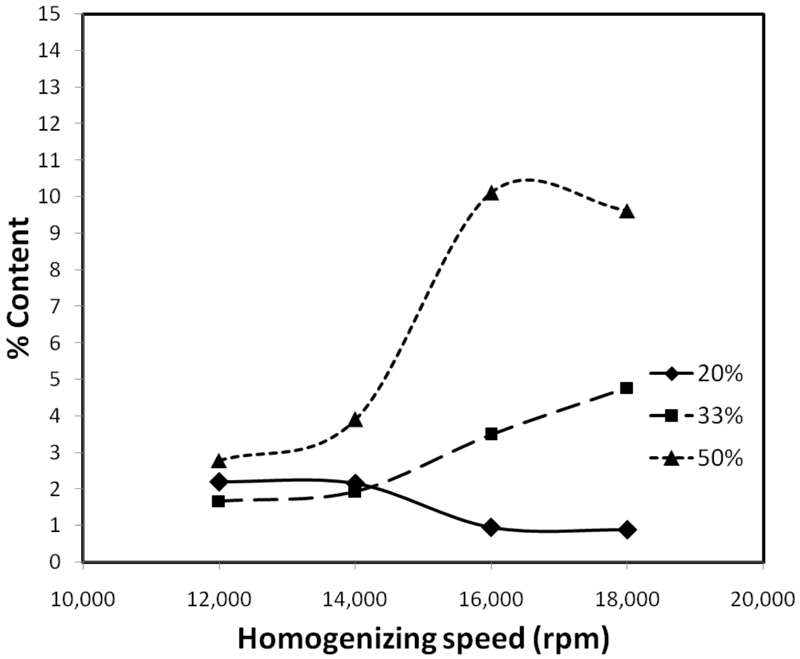


Figure 4.14 The effect of the homogenizing speed on %Content of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is (a) 20%, (b) 33% and (c) 50%.

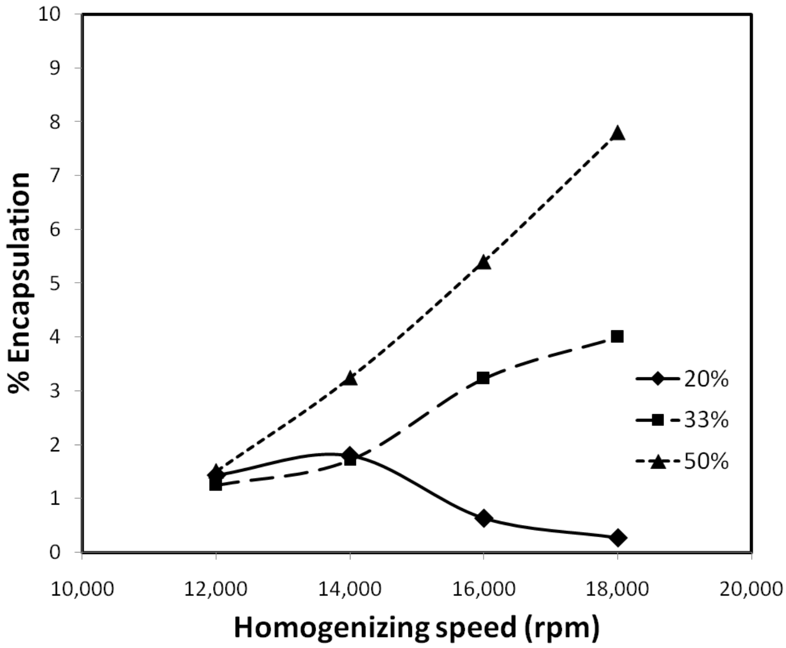


Figure 4.15 The effect of the homogenizing speed on %Encapsulation of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is (a) 20%, (b) 33% and (c) 50%.

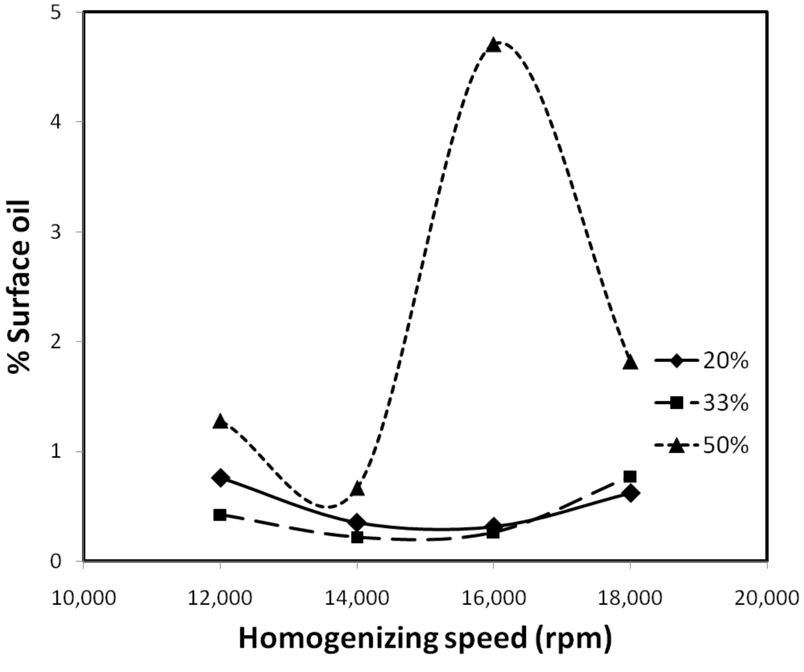


Figure 4.16 The effect of the homogenizing speed on %Surface oil of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is (a) 20%, (b) 33% and (c) 50%.

4.2.5 Effect of the homogenizing speed on energy storage and release capacity.

The energy storage and release capacity of the microcapsules are evaluated by DSC, and their heat capacity obtained from the DSC measurement are listed in Table 4.1. For the microcapsules which contain n-Octadecane 33 wt% and 50 wt% the results show that the enthalpies increases as the homogenizing speed increases, suggesting that for the high homogenizing speed the microcapsules have the high loading content of n-Octadecane due to the small emulsion droplets size which leads to good embedding of n-Octadecane in microcapsule. However, for the microcapsules which contain n-Octadecane at 20% wt the results show the enthalpies decrease as the homogenizing increases, suggesting that for the low content of n-Octadecane in microcapsule that caused by the high concentration of Na_2SiO_3 in emulsion which lead to high rate of hydrolysis and condensation as described above. This result is similar with the mole ratio of Tween 20: PCMs is 0.5:1.

Table 4.1 Melting enthalpy and the crystallization enthalpy of microcapsule at various homogenizing speed and % content of n-Octadecane.

Tween 20:PCMs molar ratio	% content of n-Octadecane	Homogenizing speed (rpm)	The heats of melting, ∆Hm (J/g)	cold crystallization, ∆Hm (J/g)
0.1:1	20%	12,000	3.11	2.94
		14,000	4.22	3.91
		16,000	1.31	1.22
		18,000	0.61	0.56
	33%	12,000	3.68	4.46
		14,000	4.06	4.99
		16,000	6.98	6.85
		18,000	8.70	8.87
	50%	12,000	3.96	4.21
		14,000	7.38	7.37
		16,000	9.02	8.11
		18,000	14.86	14.84

4.3 Effect of the homogenizing time.

4.3.1 Effect of the homogenizing time on emulsion droplet size.

The effect of homogenizing time on emulsion droplets size was investigated by Particle size analyzer. The mixture of n-Octadecane, the Tween 20 solution and the Sodium silicate solution was homogenized by a homogenizer for different homogenizing times which are 3 minutes, 5 minutes and 7 minutes.

Figure 4.17 shows that increasing the homogenizing time result in smaller emulsion droplets size owing to for long homogenizing time, the oil phase, n-Octadecane was agitated throughout by the impeller so the long homogenizing time caused the smaller emulsion droplets size. Moreover, the droplets size distribution is normal distribution for all samples. However, the emulsion droplets size decrease barely with increasing homogenizing time due to the homogenizing time which varied as 3 minutes, 5 minutes and 7 minutes not enough to show the different result.

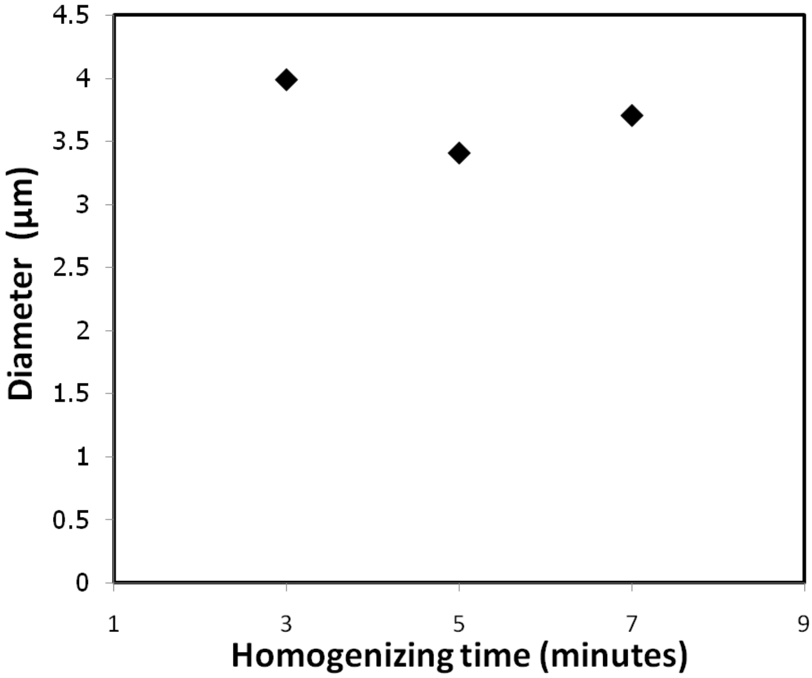
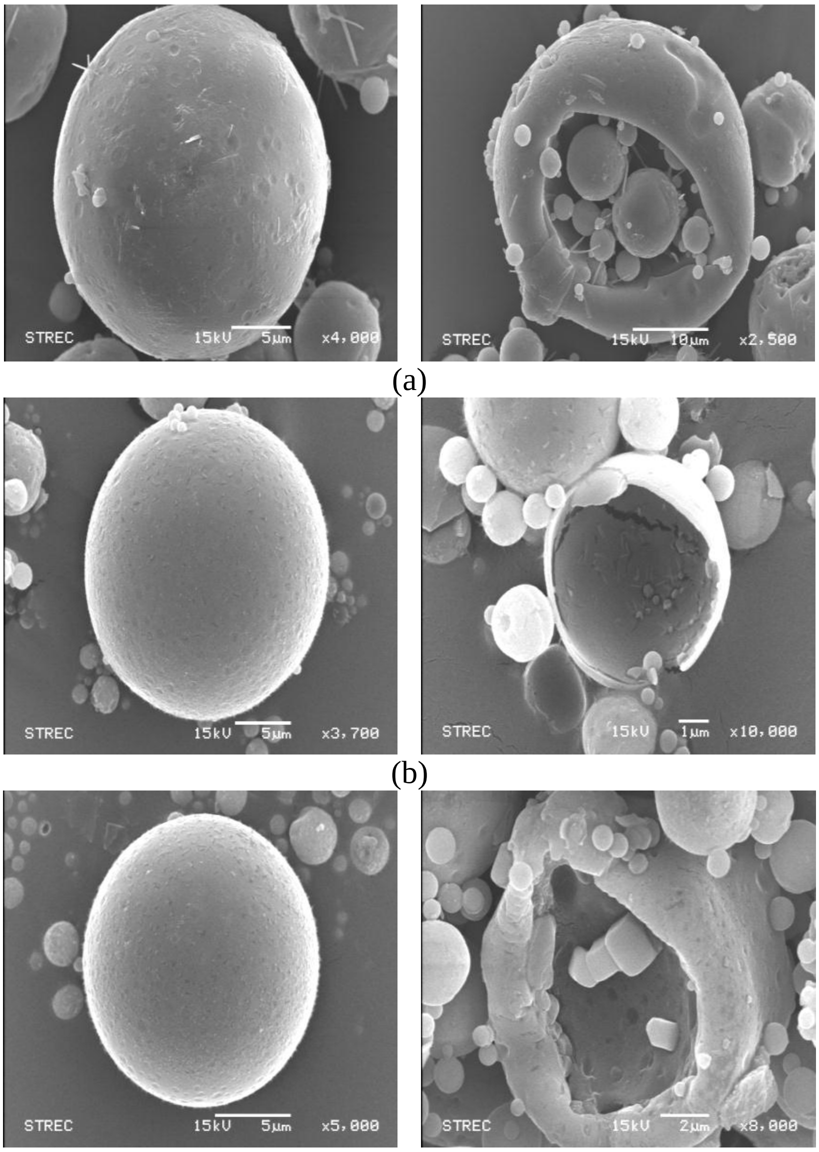


Figure 4.17 Effect of the homogenizing time on the emulsion droplet size diameter using the mole ratio of Tween 20 : PCMs which is 0.1:1, the content of the phase change material which is 20%, the homogenizing speed is 12000 rpm.

4.3.2 Effect of the homogenizing time on the morphology of microcapsule.

Figures 4.18 shows SEM micrographs of microcapsules containing PCMs which prepared at the different homogenizing time. The image shows the regular hollow spheres shape and smooth surfaces that are a result of spray drying process.



(a)

(b)

(c)

Figure 4.18 The SEM micrograph of silica microcapsules which synthesized at the molar ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 20% and the homogenizing speed is 12,000 rpm for (a) 3 minutes, (b) 5 minutes and (c) 7 minutes.

4.3.3 Effect of the homogenizing time on the retention of n-Octadecane.

Figure 4.19 shows the effect of the homogenizing time on %Total retention, %Retention in and %Retention out. The results show that %Total retention, %Retention in and %Retention out of samples which prepared at the homogenizing time at 3 minutes, 5 minutes and 7 minutes are the same. Although the emulsion droplets size of sample that prepared with homogenizing time 3 minutes are smaller than the emulsion droplets size of sample 5 minutes and 7 minutes due to the homogenization process, at first the suspension of oil phase in a water phase gives the droplet formation. For a long homogenizing time, the droplets can coalesce and form into the bulk liquid-phase again. For that reason, a long homogenizing time leads to a decrease in encapsulation efficiency [7].

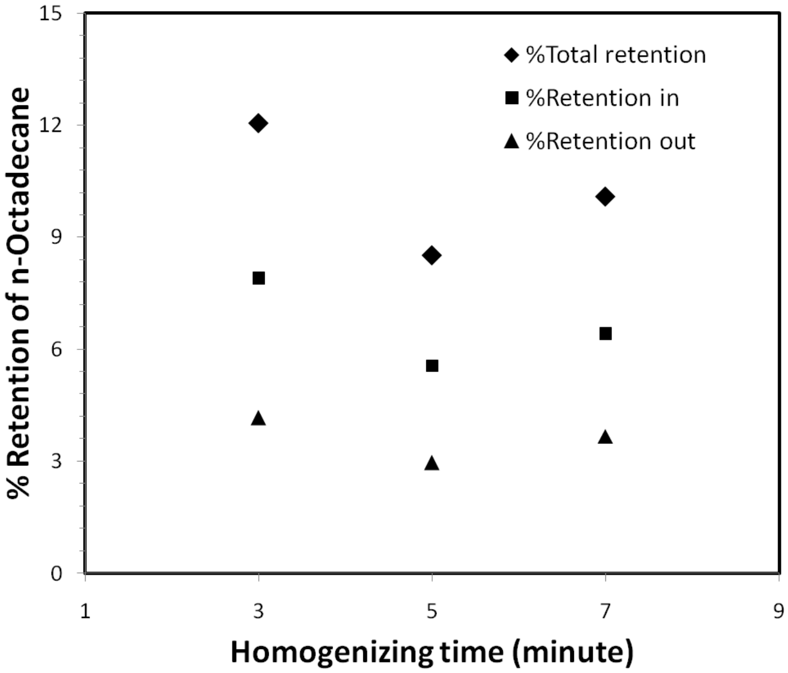


Figure 4.19 The effect of the homogenizing time on the retention of n-Octadecane of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the n-Octadecane loading which is 20% wt and the homogenizing speed is 12,000 rpm.

4.3.4 Effect of the homogenizing time on the of n-Octadecane content in microcapsule.

Figure 4.20 shows the effect of the homogenizing time on %Content, %Encapsulation and %Surface oil. The results show that %Total retention, %Retention in and %Retention out of samples which prepared at the homogenizing time at 3 minutes, 5 minutes and 7 minutes are the same. These results are similar with the %Total retention, %Retention in and %Retention out as showed in Figure 4.19.

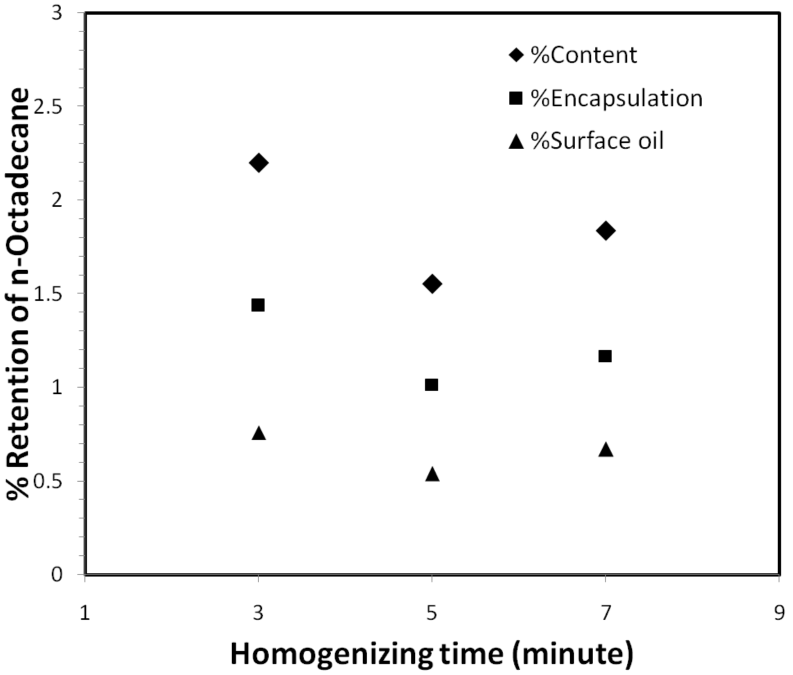


Figure 4.20 The effect of the homogenizing time on the n-Octadecane content in microcapsule, which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the content of the phase change material which is 20% wt and the homogenizing speed is 12,000 rpm.

4.3.5 Effect of the homogenizing time on energy storage and release capacity.

The heat capacities of microcapsules which prepared at the homogenizing speed 12,000 rpm and the n-Octadecane loading is 20% were investigated. The results obtained from the DSC measurement are listed in Table 4.2. The results show that the enthalpies are the same as the homogenizing time increases. Because of the samples were prepared at n- Octadecane loading 20% so the smaller emulsion droplets size does not have more affect to the enthalpies as described in 4.2.3.

Table 4.2 Melting enthalpy and the crystallization enthalpy of microcapsule which synthesize at the content of the phase change material which is 20%, the molar ratio of Tween 20: PCMs which is 0.1:1and the homogenizing speed is 12,000 rpm for homogenizing time.

n-Octadecane loading	**Homogenizing time (minute)**	**The heats of melting, ∆Hm (J/g)**	**cold crystallization, ∆Hm (J/g)**
20%	3	3.11	2.94
	5	3.13	3.18
	7	2.93	3.21

4.4 Effect of the PCMs loading (wt% of total solid).

4.4.1 Effect of the PCMs loading on emulsion droplet size.

The effect of the PCMs loading on emulsion droplet size was investigated by preparing the microcapsules at the different n-Octadecane loading 20%wt, 30%wt and 50%wt, the molar ratio of Tween 20: PCMs is 0.1:1

Figure 4.21 shows the emulsion droplets size are the same with increasing the n-Octadecane loading at the same homohenizing speed.This implies that for constant surfactant content and constant homogenizing speed, the n-Octadecane loading does not have significant affect to the emulsion droplets size.

Figute 4.22 shows a light microscope image of O/W emulsion which prepared at the mole ratio of Tween 20: PCMs which is 0.1:1 for different n-Octadecane loading. The micrographs show many small PCMs droplets of n-Octadecane were suspended as the dispersed phase throughout the continuous phase. Moreover, the droplets look similar with higher n-Octadecane loading. Due to the samples were prepared at the same homogenizing speed and the same surfactant content. Therefore, the shear rate is the same that result in the droplets size are the same.

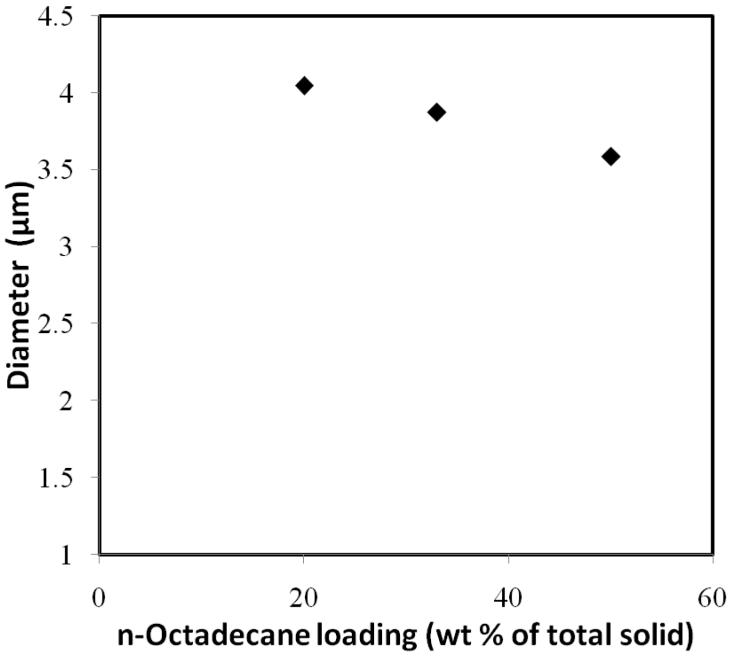
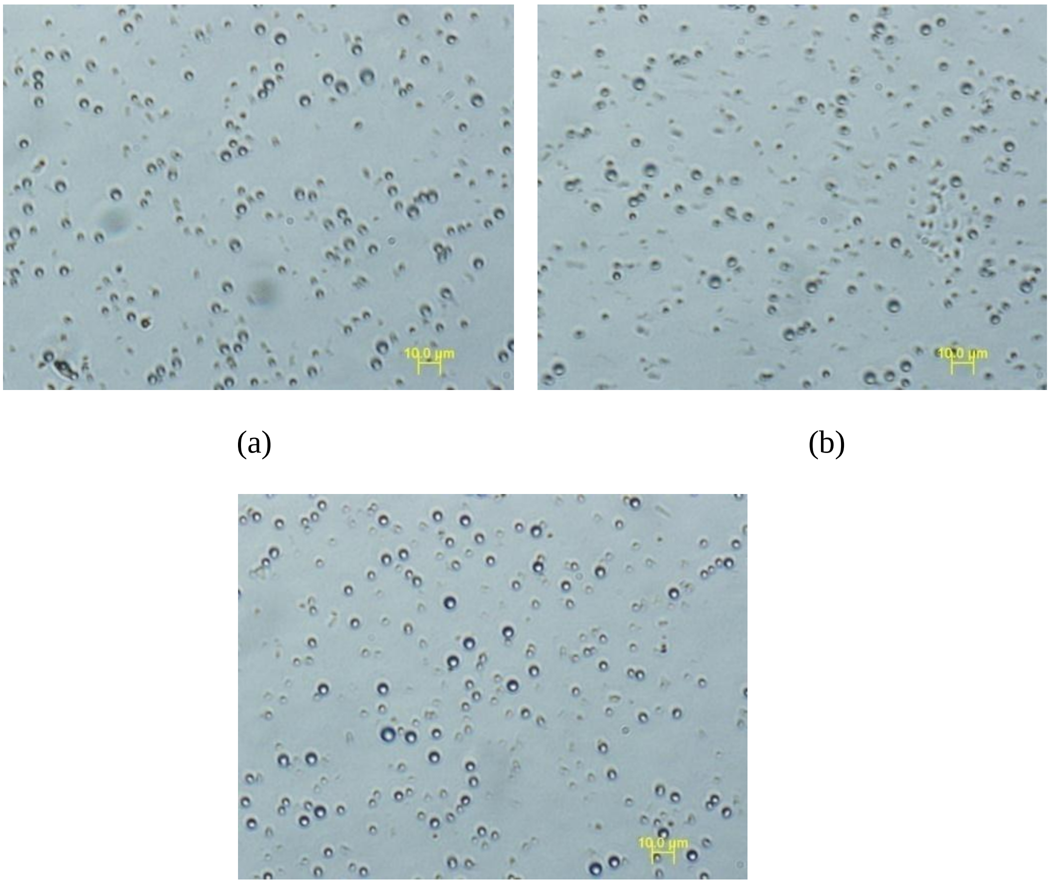


Figure 4.21 Effect of the n-Octadecane loading on the emulsion droplet size diameter using the mole ratio of Tween 20 : PCMs which is 0.1:1, The homogenizing speed which is 12,000 rpm and 14,000 rpm.

4.4.2 Effect of the PCMs loading on the morphology of microcapsule.

Figures 4.23 shows SEM micrographs of microcapsules containing PCMs which prepared at the different PCMs loading. The image shows that the microcapsules are the hollow spheres shape and smooth surfaces that are typically generated using of spray drying process.

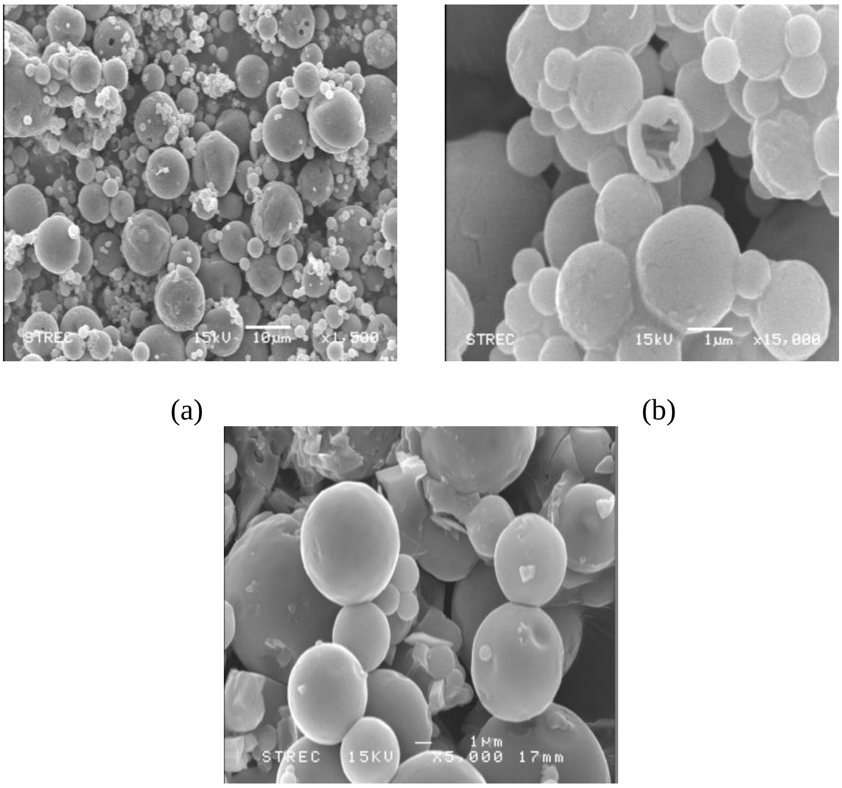
.



(a) (b)

(c)

Figure 4.22 The micrograph of the emulsion using the mole ratio of Tween 20: PCMs which is 0.1:1, the homogenizing speed is 12,000 rpm and the content of the phase change material which is (a) 20%, (b) 33% and (c) 50%.



(a) (b)

(c)

Figure 4. 23 The SEM micrograph of silica microcapsules which synthesized at the molar ratio of Tween 20 : PCMs which is 0.1:1, homogenizing speed is 12,000 rpm and The content of the phase change material which is (a) 20 wt%, (b) 33 wt%, and (c) 50 wt%

4.4.3 Effect of the PCMs loading on the retention of n-Octadecane.

Figure 4.24 The effect of the PCMs loading on the retention of n-Octadecane of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1 and the homogenizing speed is 18,000 rpm. The results show the %Total retention and %Retention in increase hardly with increasing the n-Octadecane loading. Furthermore, %Retention out is the same with increasing the n-Octadecane loading. These results due to the large amount of n-Octadecane that were embedded in the microcapsules. Moreover, The good embedding of n-Octadecane in microcapsule is a result of the small emulsion droplets size. For this sample, the small emulsion droplets size are caused by high shear rate from the homogenizing speed 18,000 rpm.

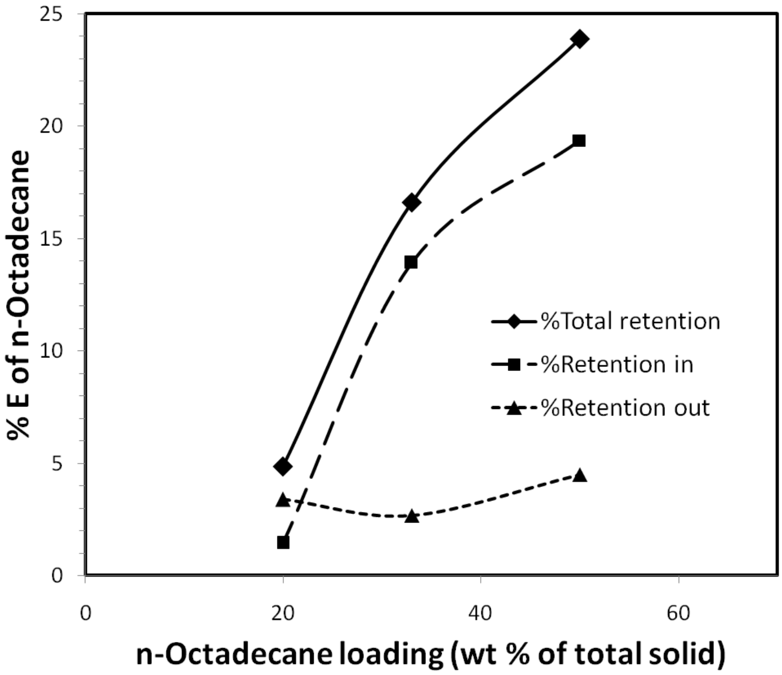


Figure 4.24 The effect of the PCMs loading on the retention of n-Octadecane of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1 and the homogenizing speed is 18,000 rpm.

4.4.4 Effect of the PCMs loading on the of n-Octadecane content in microcapsule.

Figure 4.25 shows the effect of the n-Octadecane loading on n-Octadecane content in microcapsule which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1 and the homogenizing speed is 18,000 rpm. The results show the %Content and %Encapsulation in increase dramatically with increasing the n-Octadecane loading. Furthermore, %Surface oil increases slightly with increasing the n-Octadecane loading. Because of the large amount of n-Octadecane that were embedded in the microcapsules. That is the result of high homogenizing speed which leads to the good embedding of n-Octadecane in microcapsule is a result of the small emulsion droplets size.

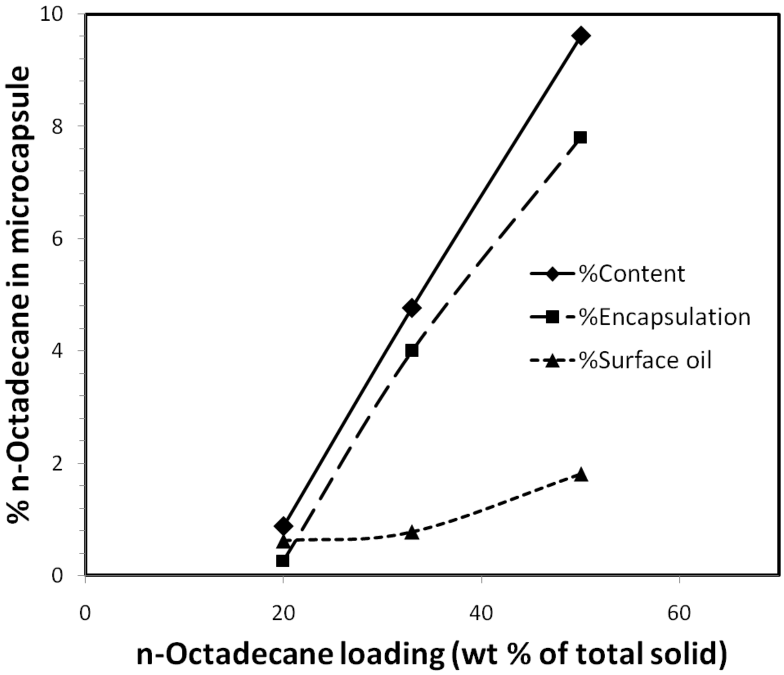


Figure 4.25 The effect of the PCMs loading on the n-Octadecane content in microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1 and the homogenizing speed is 18,000 rpm.

4.4.5 Effect of the PCMs loading on energy storage and release capacity.

The effect of the PCMs loading on energy storage and release capacity is evaluated by DSC, and their heat capacities obtained from the DSC measurement are listed in Table 4.3.

The results show that, for all homogenizing speed 14,000, 16,000 and 18,000 rpm the enthalpies increase with increasing n-Octadecane loading. These suggesting that, for the high n-Octadecane loading the microcapsules have the high content of n-Octadecane due to the small emulsion droplets size which leads to good embedding of n-Octadecane in microcapsule.

Table 4.3 Melting enthalpy and the crystallization enthalpy of microcapsule prepared using the mole ratio of Tween 20: PCMs which is 0.1:1 at various n-Octadecane loading.

Homogenizing speed (rpm)	**The weight ratio of phase change material %**	**The heats of melting, ∆Hm (J/g)**	**cold crystallization, ∆Hm (J/g)**
12,000	20	3.11	2.94
	33	3.68	4.46
	50	3.96	4.21
14,000	20	4.22	3.91
	33	4.06	4.99
	50	7.38	7.37
16,000	20	1.31	1.35
	33	6.98	6.85
	50	9.82	8.11
18,000	20	0.61	0.56
	33	8.70	8.87
	50	14.86	14.84

4.5 Effect of the surfactant content.

4.5.1 Effect of the surfactant content on emulsion droplet size.

It is widely known that the emulsifier or surfactant plays important role in an emulsion system. In this research the effect of the surfactant concentration on emulsion droplet size have been studied. From the fact that the amount of surfactant is an important factor influencing the colloidal stability because the size of the droplets, directly dispersed after primary equilibration, depends on the amount of surfactant in the emulsion progress [6]. In addition, the affect of molar ratio of Tween 20: PCMs from 0.3:1 to 1:1 were investigated. Figure 4.26 Shows the droplets size of emulsion which was prepared at the homogenizing speed 12,000 rpm. The emulsion droplets size is retains the same range with the increasing of Tween 20: PCMs molar ratio.

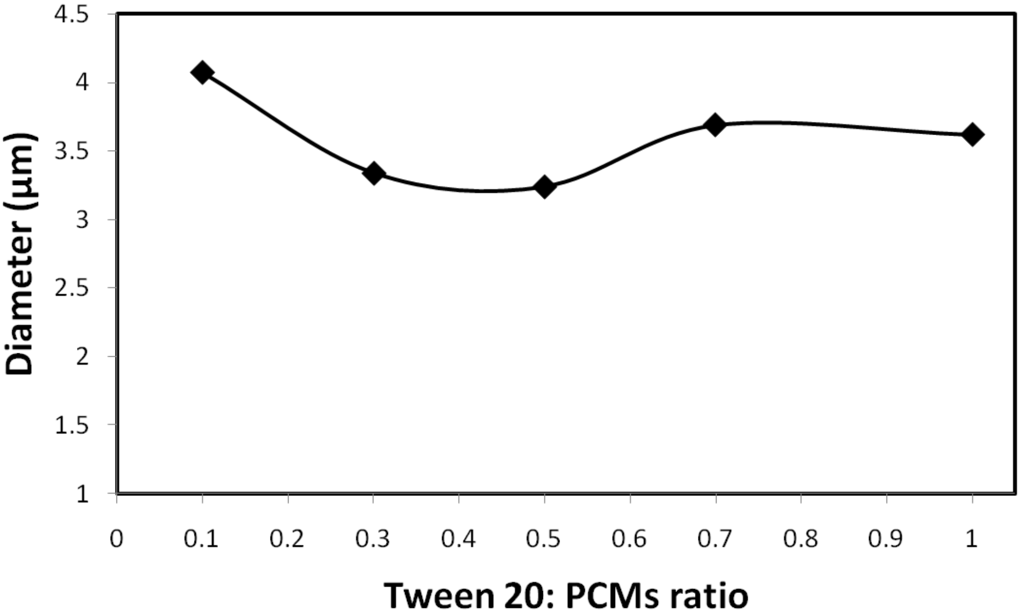


Figure 4.26 Effect of the surfactant concentration on emulsion droplet size which prepared at the homogenizing speed 12,000 rpm by various Tween 20 : PCMs molar ratio.

4.5.2 Effect of the surfactant content on the morphology of microcapsule.

Figure 4.27 shows the SEM micrograph of silica microcapsules which synthesized at the mole ratio of Tween 20 : PCMs which is (a) 0.1:1, (b) 0.5:1. The microcapsules are hollow, regular spheres shape due to the spray drying process. The n-Octadecane was embedded in the wall of capsule and method.

4.5.3 Effect of the surfactant content on the retention of n-Octadecane.

The retention of n-Octadecane at the different surfactant content is listed in Table 4.4. The results show %Total retention, %Retention in and %Retention out of the microcapsules decreases as the surfactant content (the Tween 20: PCMs molar ratio) increase. These suggest that the high surfactant content in the emulsion leads to the low content of n-Octadecane in microcapsules as the same reason described in 4.5.3. The core material, n-Octadecane were stuck in the viscous liquid film. Moreover, the results are similar with the % n-Octadecane content in microcapsule is listed in Table 4.5.

Table 4.4 The % retention of n-Octadecane at various surfactant concentrations.

n-Octadecane loading	Homogenizing speed (rpm)	Tween 20:PCMs molar ratio	%Total retention	%Retention in	%Retention out
50%	12,000	0.1:1	7	4	3
		0.5:1	11	6	5
	14,000	0.1:1	10	8	2
		0.5:1	5	4	1
	16,000	0.1:1	25	13	12
		0.5:1	9	8	1
	18,000	0.1:1	24	19	5
		0.5:1	15	12	3

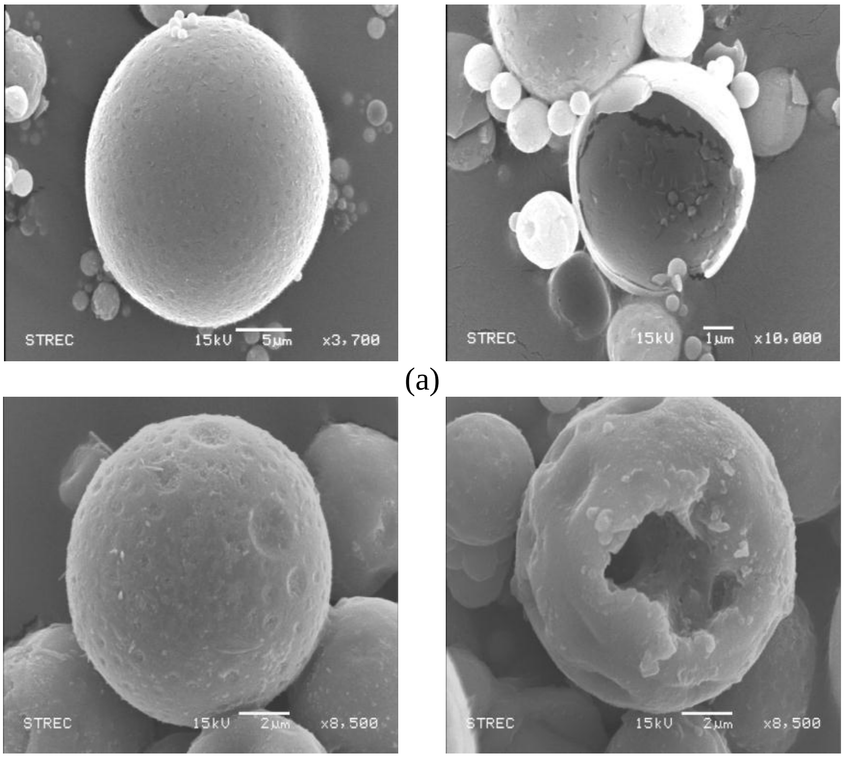
4.5.4 Effect of the surfactant content on the of n-Octadecane content in microcapsule.

Table 4.5 The % n-Octadecane contents in microcapsule at varioussurfactant concentrations.

n-Octadecane loading	Homogenizing speed (rpm)	Tween 20:PCMs molar ratio	%Content	%Encapsulation	%Surface oil
50%	12,000	0.1:1	3	2	1
		0.5:1	3	2	1
	14,000	0.1:1	4	3	1
		0.5:1	1	1	1
	16,000	0.1:1	10	5	5
		0.5:1	2	1	1
	18,000	0.1:1	10	8	2
		0.5:1	3	2	1

4.5.5 Effect of the surfactant content on energy storage and release capacity.

The energy storage and release capacity of the microcapsules at the different surfactant content are listed in Table 4.6. The results show that the enthalpies decreases as the surfactant content (the Tween 20: PCMs molar ratio) increase. These suggest that the high surfactant content in the emulsion leads to the low content of n-Octadecane in microcapsules. Because of Tween 20 property that is a viscous liquid surfactant, after the emulsion contact with the hot air, there are the viscous liquid film coat on the drying chamber and cyclone during spray drying process. The core material, n-Octadecane were stuck in the viscous liquid film.



(a)

(b)

Figure 4.27 The SEM micrograph of silica microcapsules which synthesized at the n-Octadecane loading is 20%, the homogenizing speed is 12,000 rpm and the mole ratio of Tween 20 : PCMs which is (a) 0.1:1, (b) 0.5:1.

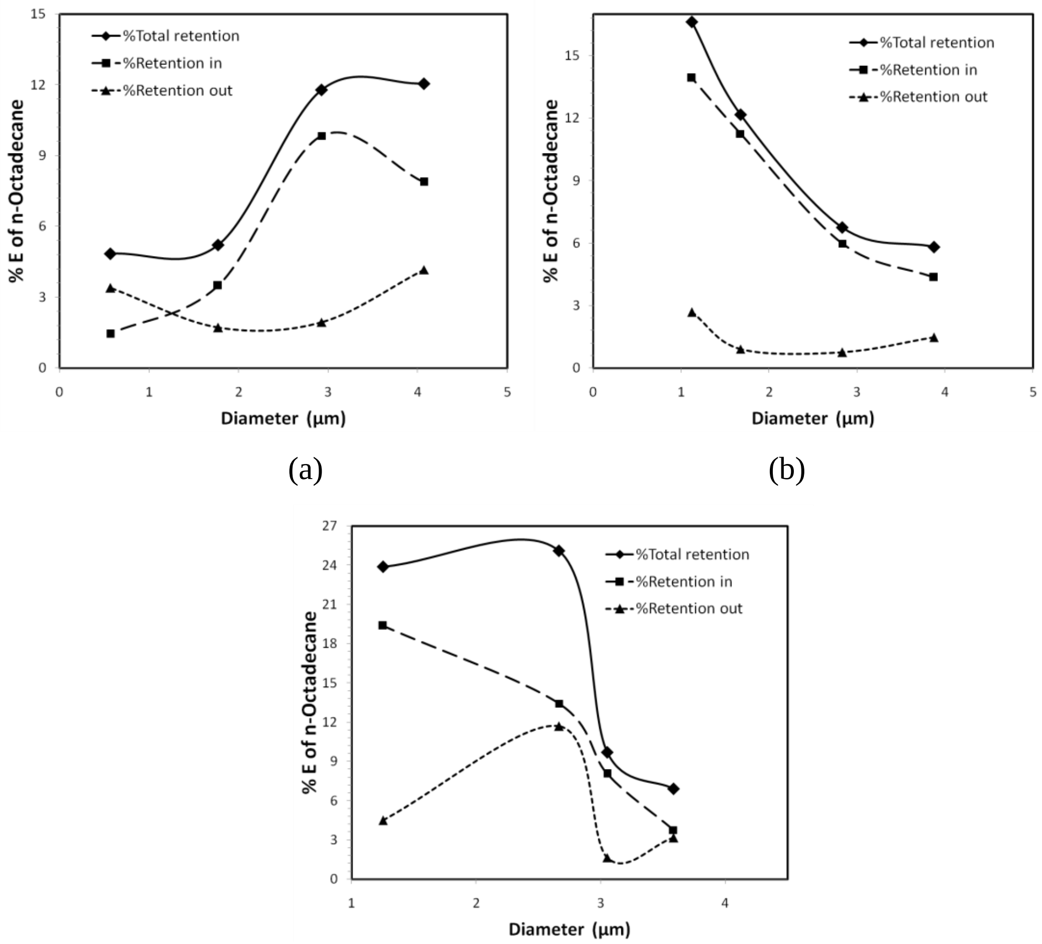
Table 4.6 Melting enthalpy and the crystallization enthalpy of microcapsule at various surfactant concentrations.

n-Octadecane loading	**Homogenizing speed (rpm)**	**Tween 20:PCMs molar ratio**	**The heats of melting, ∆Hm (J/g)**	**cold crystallization, ∆Hm (J/g)**
50%	12,000	0.1:1	3.96	4.21
		0.5:1	2.33	2.17
	14,000	0.1:1	7.38	7.37
		0.5:1	2.28	2.22
	16,000	0.1:1	9.02	8.11
		0.5:1	4.03	3.67
	18,000	0.1:1	14.83	14.84
		0.5:1	5.76	4.87

4.6 Effect of the emulsion size.

4.6.1 Effect of the emulsion size on the retention of n-Octadecane.

Figure 4.28 shows the influence of the emulsion droplet size on the retention for the sample which the n-Octadecane loading are 20 wt%, 33 wt% and 50 wt%. The results show a low %Retention, %Retention in and %Retention out at the small emulsion droplets size for -Octadecane loading are 20 wt%. However, for the sample which the n-Octadecane loading is 33 wt% and 50 wt%, the results show the retention of n-Octadecane decreases as the emulsion size increases.This implies that the small emulsion droplets size be the cause of a good retention of core material. Due to the small emulsion size leads to good retention of n-Octadecane in powder.



(a)

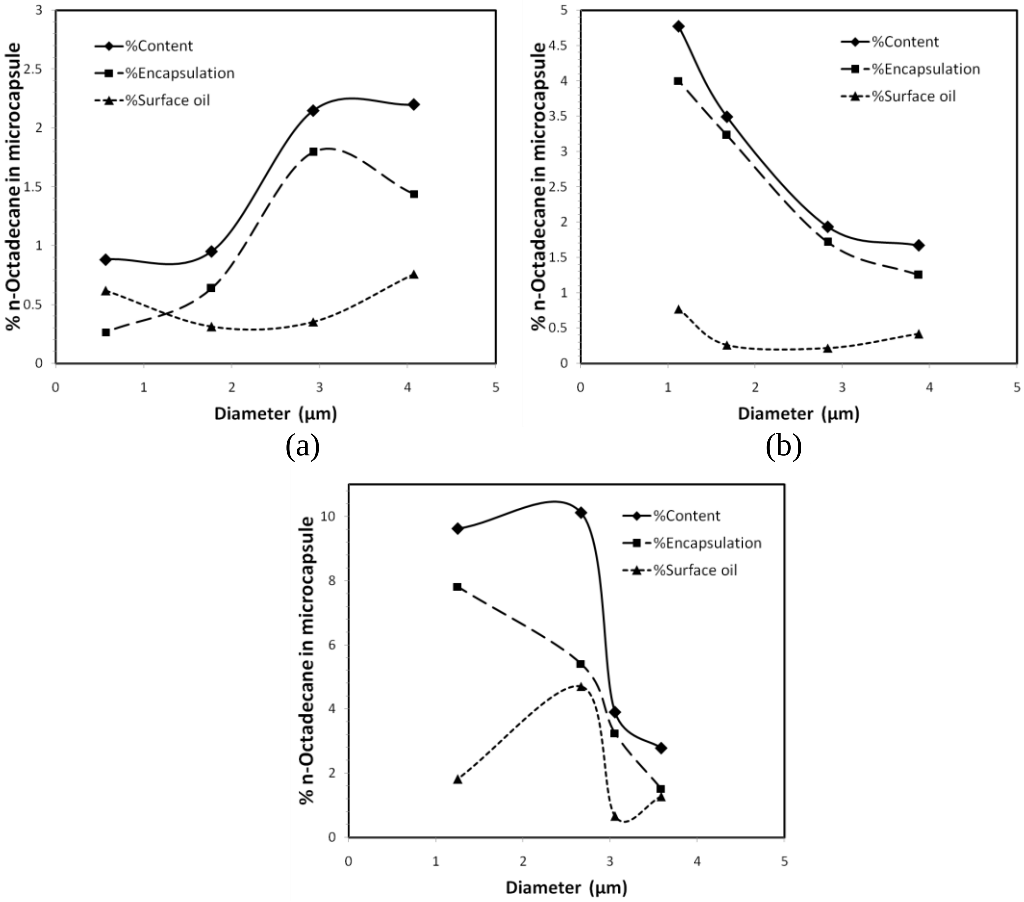
(b)

(c)

Figure 4.28 The effect emulsion size on the retention of n-Octadecane of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the n-Octadecane loading is (a) 20 wt%, (b) 33wt% and (c) 50 wt%.

4.6.2 Effect of the emulsion size on the of n-Octadecane content in microcapsule.

The effect of the feed emulsion droplet size on the n-Octadecane content in microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the n-Octadecane loading is 20 wt%, 33 wt% and 50 wt% were showed in Figure 4.29. Figure 4.29 shows the %Content and %Encapsulation decrease with decreasing emulsion droplets size for sample which the n-Octadecane 20wt% but show the different result for n-Octadecane loading 33 wt% and 50 wt% that a smaller emulsion droplets size leads to a high %Content of n-Octadecane.



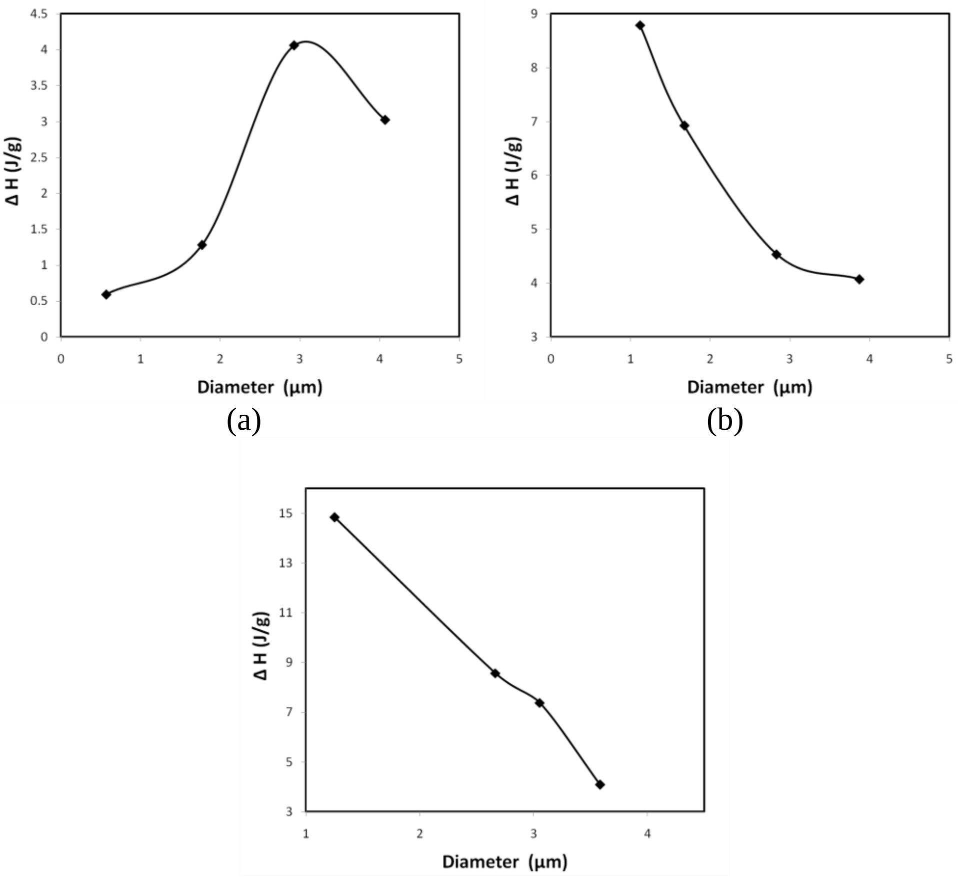
(a) (b)

(c)

Figure 4.29 The effect of the emulsion size on the n-Octadecane content in microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1, the n-Octadecane loading is (a) 20 wt%, (b) 33wt% and (c) 50 wt%.

4.6.3 Effect of the emulsion size energy storage and release capacity.

Figure 4.30 show the heat capacity increases as the emulsion size decreases for the sample which the n-Octadecane loading is 33 wt% and 50 wt%, This implies that the small emulsion droplets size be the cause of a good embed of core material. However, the result also show heat capacity increases as the emulsion size increases for the sample which the n-Octadecane loading is 20 wt%. This is a result of the high rate of gelation in this condition, longtime aging of silica sol gel as a water phase in emulsion as described in 4.2.4. These results agree with S.Kornbongkotmas who represented that long time of sol gel result in the microcapsules have low energy storage.



(a) (b)

(c)

Figure 4.30 Effect of the emulsion size on the heat capacity of microcapsules which prepared using the mole ratio of Tween 20: PCMs which is 0.1:1 the n-Octadecane loading is (a) 20 wt%, (b) 33wt% and (c) 50 wt%.

The result of the effect of emulsion size on the retention of n-Octadecane, the content of n-Octadecane and the heat capacity of microcapsule is conform to the result of the effect of homogenizing speed because the small emulsion droplet size led from high homogenizing speed. For the sample which the n-Octadecane loading is 20 wt%, the low ratio of H_2O/Na_2SiO_3 causes the fast gelation that induces the low retention of n-Octadecane as described in 4.2.3.

4.7 Thermal stability of microcapsule.

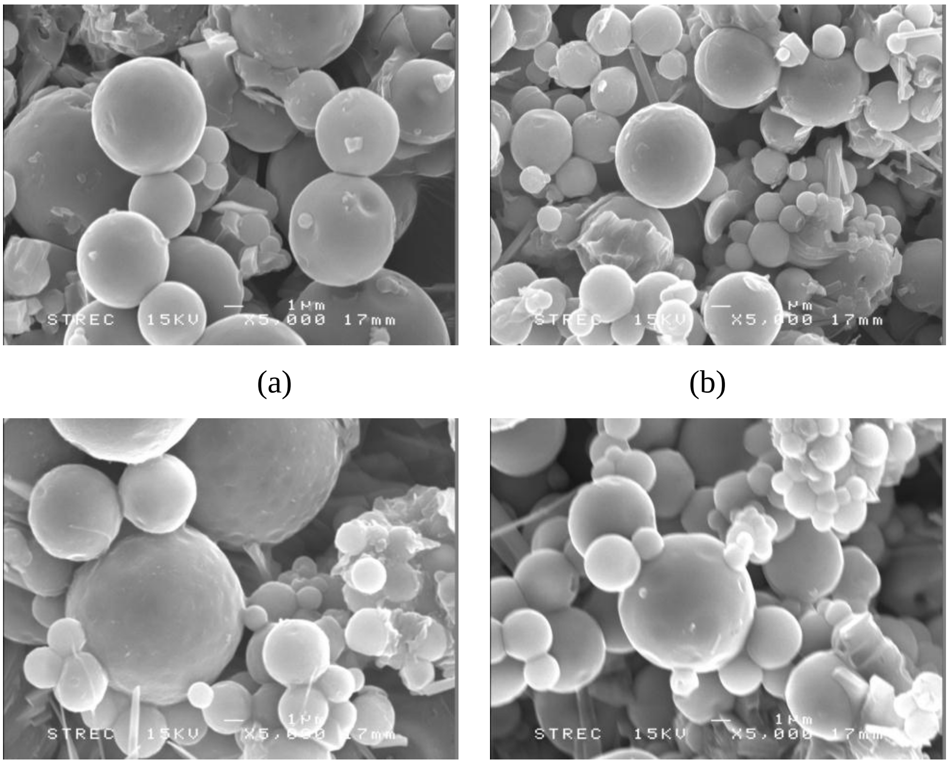
4.7.1 The morphology of dried microcapsule.

After drying of the microcapsules at 100°C, 200°C for 5 minutes and 30 minutes, the surface structure of dried microcapsules were the same as show in Figure 4.31. This implied that the microcapsules have stability in shape for high temperature.

4.7.2 The energy storage and release capacity of dried microcapsule.

In this study, the PCMs microcapsules were successfully prepared via sol gel process in emulsion and spray drying process. The stability of microcapsule is an important for using PCMs microcapsule in many applications of heat energy storage. The thermal stability of the microcapsules was investigated by drying the microcapsules at 100°C and 200 °C for 5minutes and 30 minutes. After that the dried microcapsules were characterized the enthalpies by DSC and the results show in Table 4.7 below.

Table 4.7 show that the heat capacity of microcapsule decrease barely after drying. In addition, the heat capacity of microcapsules decrease as the drying temperature and the drying time increase. Due to the fact that when the drying process occurred some PCMs within microcapsules melted and leak from the pore of microcapsules. It implies that the loss of PCMs within the microcapsules significantly depends on the drying temperature and drying time.



(a) (b)

(c) (d)

Figure 4.31 The SEM micrograph of silica microcapsules which dried (a) 100°C for 5 minutes, (b) 100°C for 30 minutes, (c) 200°C for 5 minutes and (d) 200 °C for 30 minutes.

Table 4.7 Melting enthalpy and the crystallization enthalpy of microcapsules after drying.

Drying temperature (°C)	**Drying time (min)**	**The heats of melting, ∆Hm (J/g)**	**cold crystallization, ∆Hm (J/g)**
100	0	14.01	13.77
	5	11.41	10.32
	30	11.0	10.50
200	0	14.01	13.77
	5	10.48	10.90
	30	9.82	9.93

CHAPTER V

CONCLUSIONS

5.1 Conclusions

This research has been carried out on the preparation and estimation properties and performance of microencapsulated n-Octadecane prepared by sol-gel and spray drying process. From the results of this study, the conclusion of this research can be described as follows

The microencapsulation of n-Octadecane with silica from sodium silicate successfully prepared in O/W emulsion via sol-gel and spray drying process. The microcapsule is a hollow, regular spheres shape and the n-Octadecane was embedded in the wall of microcapsule.

The objective of this study is to find the conditions which emulsion droplets size is small, a small size is important for high PCMs content in the microcapsule. The results of this work show the homogenizing speed plays important role in the emulsion droplets size. In addition, the stability of emulsion is depending on the amount of surfactant, the high content of surfactant in emulsion result in more stability of emulsion but leads to low retention of n-Octadecane in microcapsule.

The heat capacity of microcapsule increases as the the n-Octadecane loading increases and also increases as the homogenizing speed increases for the n-Octadecane loading 33 and 50%wt of total solid weight. The maximum encapsulation efficiency is 7.8%, retention is 19% and the average latent heat of microencapsulated n-octadecane is 14.85 J/g. were found at the homogenizing speed is 18,000 rpm, n-Octadecane loading is 50 wt% and the mole ratio of surfactant and phase change material 0.1:1. Furthermore, the microcapsules 1. have the thermal stability at 200°C and 30 minutes.

5.2 Recommendations

Recommendations for the future work, based on the results of this work, are following.

1. As a result of high surfactant content in the emulsion leads to the low content of n-Octadecane in microcapsules because of Tween 20 property that is a viscous liquid surfactant, after the emulsion contact with the hot air, there are the viscous liquid film coat on the drying chamber and cyclone during spray drying process. The core material, n-Octadecane were stuck in the viscous liquid film. Therefore, the other surfactant which is a solid surfactant needs to be investigated.

2. The spray drying process conditions play important role in the morphology of microcapsules. The morphology of microcapsule affects on the encapsulation efficiency so the spray drying process conditions need to be investigated.

REFERENCES

[1] Tyagia, V.V., Kaushika, S.C., Tyagib, S.K., and Akiyamac, T. Development of phase change materials based microencapsulated technology for buildings: A review. *Renewable and Sustainable Energy Reviews* 15,2(2011): 1373-1391.

[2] Mondal, S. Phase change materials for smart textiles – An overview. *Applied Thermal Engineering* 28,11-12(2008): 1536-1550.

[3] Zhang, Y.P., Lin, K.P., Yang, R., Di, H.F., and Jiang, Y. Preparation, thermal performance and application of shape-stabilized PCM in energy efficient buildings. *Energy and Buildings* 38,10(2006): 1262-1269.

[4] Sánchez, L., Sánchez, P., Lucas, A., Carmona, A., and Rodríguez, J. Microencapsulation of PCMs with a polystyrene shell. *Colloid & Polymer Science* 285,(2007): 1377-1385.

[5] Sharma, A., Tyagi, V.V., Chen, C.R., and Buddhi, D. Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable Energy Reviews* 13,2(2009): 318-345.

[6] Zhang, H., Wang, X., and Wu, D. Silica encapsulation of n-octadecane via sol–gel process: A novel microencapsulated phase-change material with enhanced thermal conductivity and performance. *Journal of Colloid and Interface Science* 343,1(2009): 246-255.

[7] Hawlader, M.N.A., Uddin, M.S., and Khin, M.M. Microencapsulated PCM thermal-energy storage system. *Applied Energy* 74,1-2(2003): 195-202.

[8] Bay´es-Garcı´a, L., et al. Phase Change Materials (PCM) microcapsules with different shell compositions: Preparation, characterization and thermal stability. *Solar Energy Materials & Solar Cells* 94,7(2010): 1235-1240.

[9] Jin, Y., Lee, W., Musina, Z., and Ding, Y. A one-step method for producing microencapsulated phase change materials. *Particuology* 8,6(2010): 588-590.

[10] Miao, C.Y., Yao, Y.W., Tang, G.Y., and Weng, D. Preparation and characterization of silica microcapsules containing butyl-stearate via sol-gel method. *Transactions of Nonferrous Metals Society of China* 17(2007): 1018-1021.

[11] Fujiwara, M., Shiokawa, K., Tanaka, Y., and Nakahara, Y. Preparation and formation mechanism of silica microcapsules (hollow sphere) by water/oil/water interfacial reaction. *International Journal of Pharmaceutics* 16,25(2004): 5420-5426.

[12] Miao, C.Y., Yao, Y.W., Tang, G.Y., and Weng, D. Preparation of shape-stabilized phase change materials as temperature-adjusting powder. *Frontiers of Materials Science China* 1,3(2007): 284-287.

[13] Kornbongkotmas, S. *Microencapsulation of phase change material with silica by spray drying process*. Master's Thesis, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 2011.

[14] Pasupathy, A., et al. Phase change material-based building architecture for thermal management in residential and commercial establishments. *Renewable and Sustainable Energy Reviews* 12,1(2008): 39-64.

[15] Ravikumar, M., and Srinivasan, P. Phase change material as a thermal energy storage material for cooling of building. *Journal of Theoretical and Applied Information Technology*, (2004-2008): 503-511.

[16] Agyenim, F., Hewitt, N., Eames, P., and Smyth, M. A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). *Renewable and Sustainable Energy Reviews* 14,2(2010): 615-628.

[17] Zawrah, M., El-Kheshen, A., and Abd-El-Aal, M. Facile and economic synthesis of silica nanoparticles. *Journal of Ovonic Research* 5,5(2009): 129-133.

[18] Zuidam, N., and Nedovic´, V. *Encapsulation Technologies for Active Food Ingredients and Food Processing*. Springer, 2010.

[19] Wikipedia. *Spray Drying* [Online]. 2011. Available from: http://en.wikipedia.org/wiki/Spray_drying [2011, July 21].

[20] Benita , S. *Microencapsulation : methods and industrial applications*. New York : Marcel Dekker Inc, 1996.

[21] Microtek Laboratories inc. *Technical Overview: Microencapsulation* [Online]. 2011. Available from: http://www.microteklabs.com/technical_overview.html [2011, July 21]

[22] Sarier, N., and Onder, E. The manufacture of microencapsulated phase change materials suitable for the design of thermally enhanced fabrics. *Thermochimica Acta* 452,2(2007): 149-160.

[23] Mathiowitz, E., et al. *Microencapsulation* [Online]. 2011. Available from : http://www.ciq.uchile.cl/operaciones/liberacion/bibliografia/microencapsulation%20to%20mucosal%20drug%20delivery.pdf [2011, July 22]

[24] Cho, J.S., Kwon, A., and Cho, C.G. Microencapsulation of octadecane as a phase-change material by interfacial polymerization in an emulsion system. *Colloid & Polymer Science* 280,3(2002): 260-266.

[25] Zhang, H., and Wang, X. Fabrication and performances of microencapsulated phase change materials based on n-octadecane core and resorcinol-modified melamine–formaldehyde shell. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 332,2-3(2008): 129-138.

[26] Onder, E., Sarier, N., and Cimen, E. Encapsulation of phase change materials by complex coacervation to improve thermal performances of woven fabrics. *Thermochimica Acta* 467,1-2(2008): 63-72.

[27] Sarı, A., Alkan, C., Karaipekli, A., and Uzun, O. Microencapsulated n-octacosane as phase change material for thermal energy storage. *Solar Energy* 83,10(2009): 1757-1763.

[28] Fang, G., Chen, Z., and Li, H. Synthesis and properties of microencapsulated paraffin composites with SiO_2 shell as thermal energy storage materials. *Chemical Engineering Journal* 163,1-2(2010): 154-159.

[29] Chang, C.C., Tsai, Y., Chiu, J., and Chen, H. Preparation of phase change materials microcapsules by using pmma network-silica hybrid shell via sol-gel process. *Journal of Applied Polymer Science* 112,3(2009): 1850-1857.

[30] Kortesuo, P., et al. In vitro evaluation of sol–gel processed spray dried silica gel microspheres as carrier in controlled drug delivery. *International Journal of Pharmaceutics* 200,2(2000): 223-229.

[31] Othman, A.S. *Study on emulsion stability and chemical demulsification characteristics*. Bachelor's Thesis, Faculty of Chemical & Natural Resources Engineering, University Malaysia, 2009.

[32] Ngenda, T.N. The effect of type and concentration of surfactant on stability and rheological properties of explosive emulsion. *I CPUT Theses& Dissertations,* (2009): 63.

[33] Myers, D. *Surfactant Science and Technology*. Canada: A john wiley & sons, Inc publication, 2006.

[34] Srirama, M. DETERGENTS A guide to the propertiesand uses of detergents in biological systems. *Calbiochem-Novabiochem Corporation*, 2001

[35] Gurav, J., Venkateswara, A., Parvathy, A., Nadargi, D.Y., and Bhagat S.D. Physical properties of sodium silicate based silica aerogels prepared by single step sol–gel process dried at ambient pressure. *Journal of Alloys and Compounds* 476,1-2(2009): 397-402.

[36] Nandiyanto, A.B.D., and Okuyama, K. Progress in developing spray-drying methods for the production of controlled morphology particles: From the nanometer to submicrometer size ranges. *Advanced Powder Technology* 22,1(2011): 1-19.

[37] Capek, I. Degradation of kinetically-stable o/w emulsions. *Advances in Colloid and Interface Science* 107,2-3(2004): 125-155.

[38] Khin, M.M. *Encapsulation of phase change materials (pcms) for heat storage.* Master's Thesis, Department of Chemical and environmental Engineering , Faculty of Engineering, National University of Singapore, 2003.

[39] Soottitantawat, A., Yoshii, H., Furuta, T., Ohkawara, M., and Linko, P. Microencapsulation by spray drying: influence of emulsion size on the retention of volatile compounds. *Journal of Food Science* 68,7(2003): 2256-2262.

[40] Klein, L.C. Sol–gel processing of silicates. *Annual Review Of Materials Science* 15,(1985): 227-248.

[41] Tonon, R., Brabet, C., and Hubinger, M. Influence of process conditions on the physicochemical properties of acai (Euterpe oleraceae Mart.) powder produced by spray drying. *Journal of Food Engineering* 88,3(2008): 411-418.

APPENDICES

APPENDIX A

Calculations

1. Calculation of the retention and n-Octadecan content in microcapsule.

1.1. $\%\text{Total retention} = \dfrac{\text{Remained PCMs}}{\text{Added PCMs}} \times 100$

1.2. $\%\ \text{Retention in microcapsule} = \dfrac{\text{Remained PCMs within microcapsule}}{\text{Added PCMs}} \times 100$

1.3. % Retention out of microcapsule = %Total retention - % Retention in microcapsule

1.4. $\%\text{Content} = \dfrac{\text{Remained PCMs}}{\text{Total solid}} \times 100$

1.5. $\%\text{Encapsulation} = \dfrac{\text{PCMs within microcapsule}}{\text{Total solid}} \times 100$

1.6. %Surface oil = %Content - %Encapsulation

2. Effect of homogenizing speed.

Table A. 1 The n-Octadecane contents in microcapsule at various homogenizing speed.

Homogenizing speed (rpm)	**%Content**	**%Encapsulation**	**%Surface oil**
12,000	2.79	1.51	1.28
14,000	3.90	3.24	0.66
16,000	10.10	5.40	4.71
18,000	9.62	7.80	1.81

Table A. 2 The % Retention in microcapsule at various homogenizing speed.

Homogenizing speed (rpm)	**% Total retention**	**% Retention in microcapsule**	**% Retention out of microcapsule**
12,000	6.92	3.75	3.17
14,000	9.69	8.04	1.65
16,000	25.10	13.41	11.68
18,000	23.88	19.37	4.51

3. Effect of homogenizing time.

Table A. 3 The n-Octadecane contents in microcapsule at various homogenizing time.

Homogenizing time (time)	%Content	%Encapsulation	%Surface oil
3	2.20	1.44	0.76
5	1.56	1.01	0.54
7	1.84	1.16	0.67

Table A. 4 The % Retention in microcapsule at various homogenizing time.

Homogenizing time (minute)	% Total retention	% Retention in microcapsule	% Retention out of microcapsule
3	12.05	7.88	4.16
5	8.53	5.57	2.96
7	10.08	6.40	3.68

4. Effect of n-Octadecane loading

Table A. 5 The n-Octadecane contents in microcapsule at various n-Octadecane loading.

% n-Octadecane loading	%Content	%Encapsulation	%Surface oil
20	0.88	0.26	0.62
33	4.77	3.99	0.77
50	9.62	7.80	1.81

Table A. 6 The % Retention in microcapsule at various n-Octadecane loading.

% n-Octadecane loading	% Total retention	% Retention in microcapsule	% Retention out of microcapsule
20	4.83	1.44	3.39
33	16.61	13.93	2.69
50	23.88	19.37	4.51

APPENDIX B

DSC thermogram of microcapsules

1. The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 20% and the various homogenizing speed.

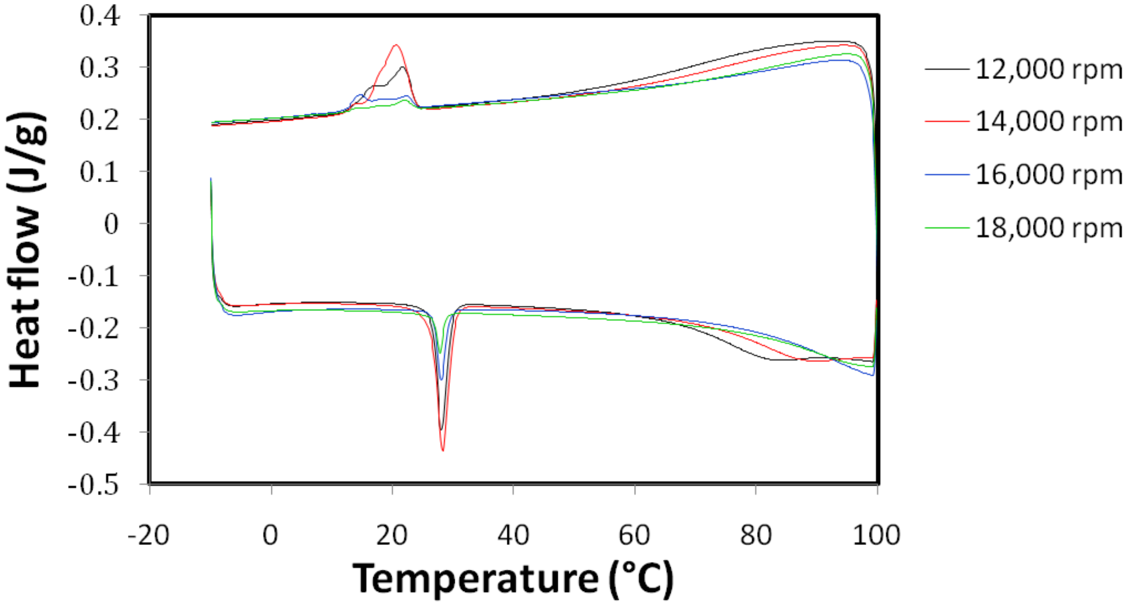


Figure A.1 The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 20% and the various homogenizing speed.

2. The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 33% and the various homogenizing speed.

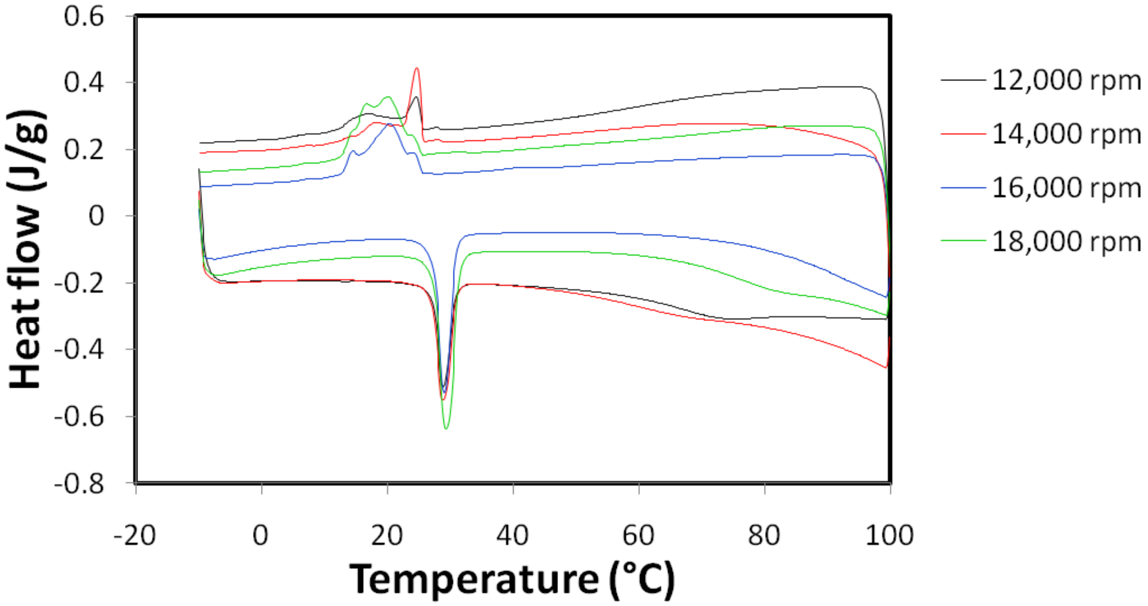


Figure A.2 The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 33% and the various homogenizing speed.

3. The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 50% and the various homogenizing speed.

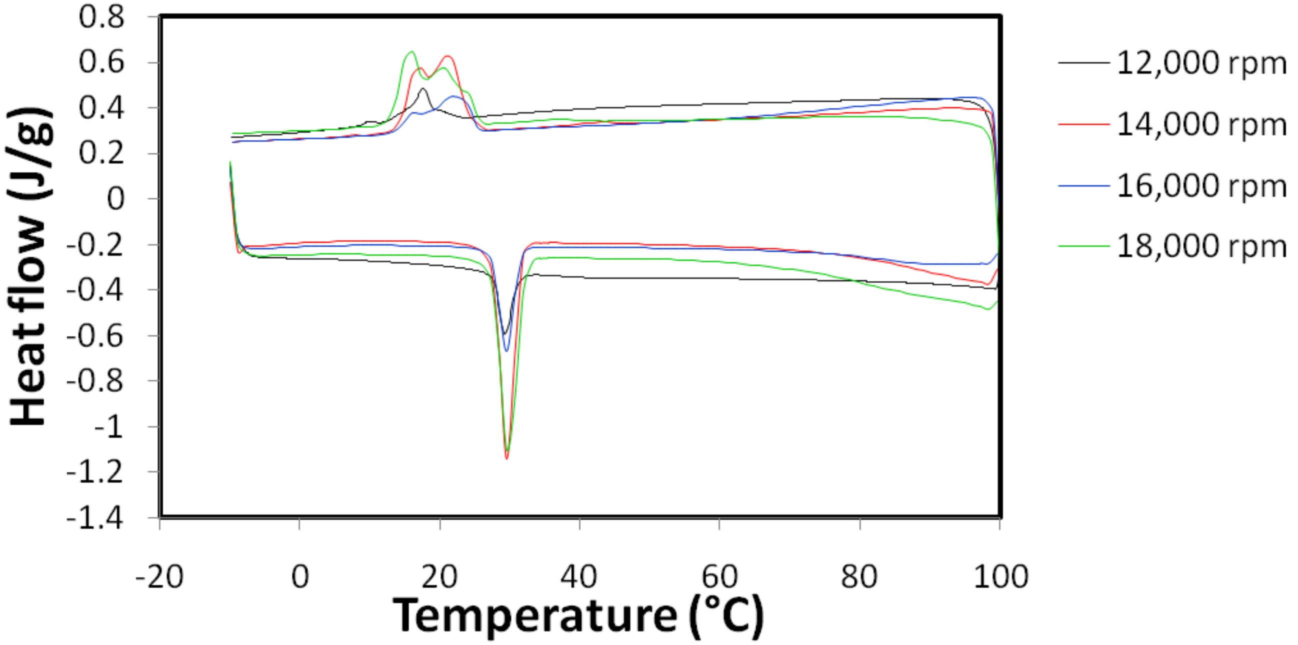


Figure A.3 The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.1:1, The content of the phase change material which is 50% and the various homogenizing speed.

4. The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.5:1, The content of the phase change material which is 20% and the various homogenizing speed.

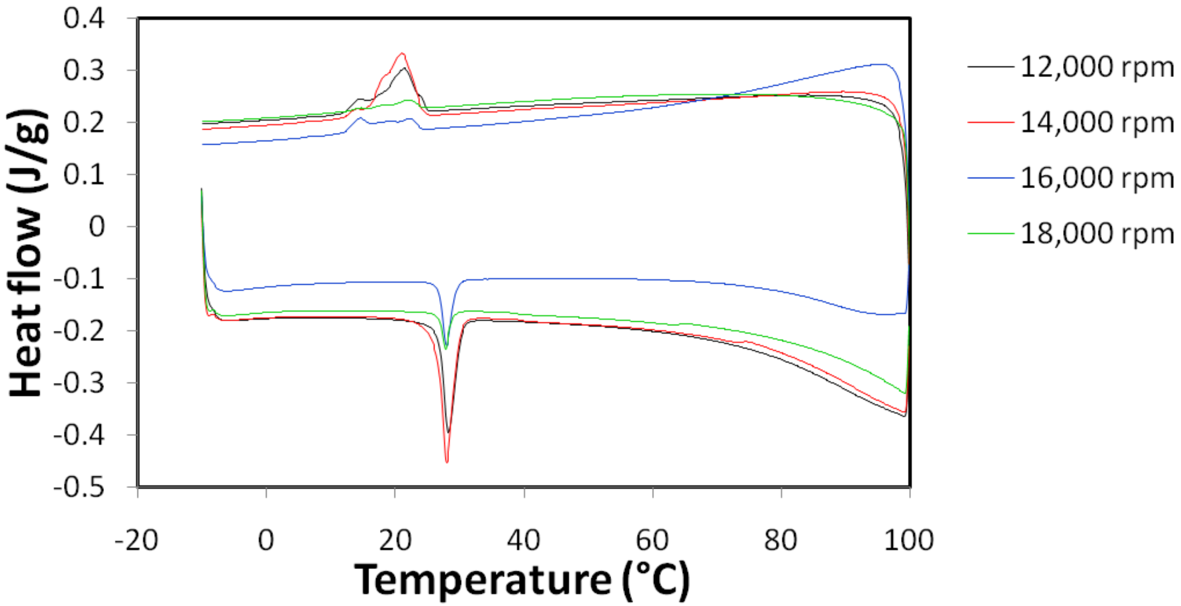


Figure A.4 The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.5:1, The content of the phase change material which is 20% and the various homogenizing speed.

5. The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.5:1, The content of the phase change material which is 33% and the various homogenizing speed.

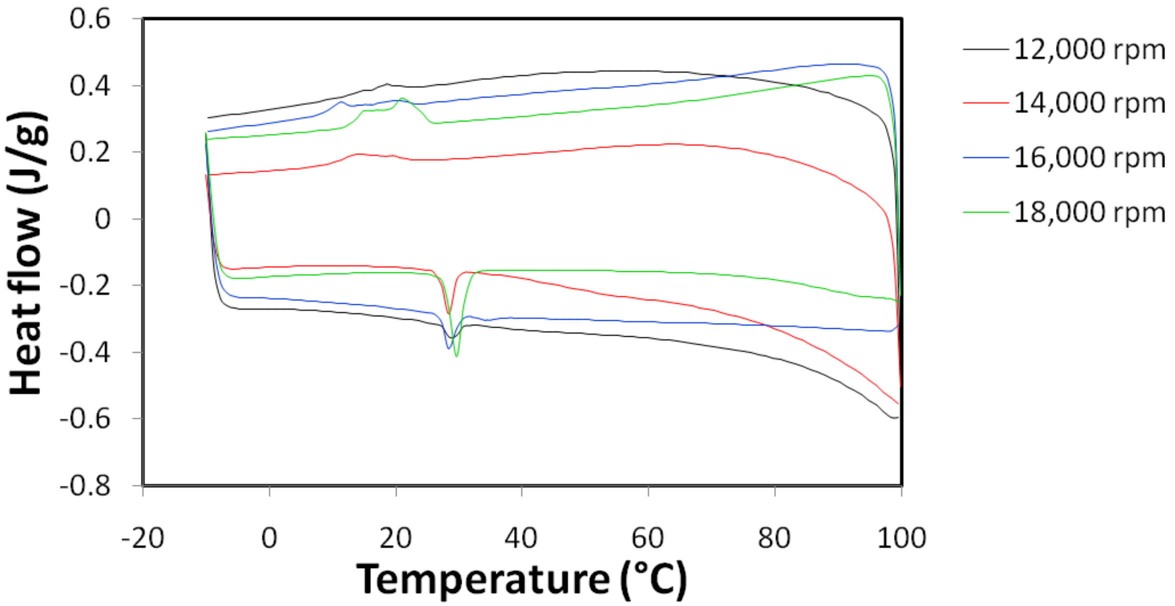


Figure A.5 The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.5:1, The content of the phase change material which is 33% and the various homogenizing speed.

6. The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.5:1, The content of the phase change material which is 50% and the various homogenizing speed.

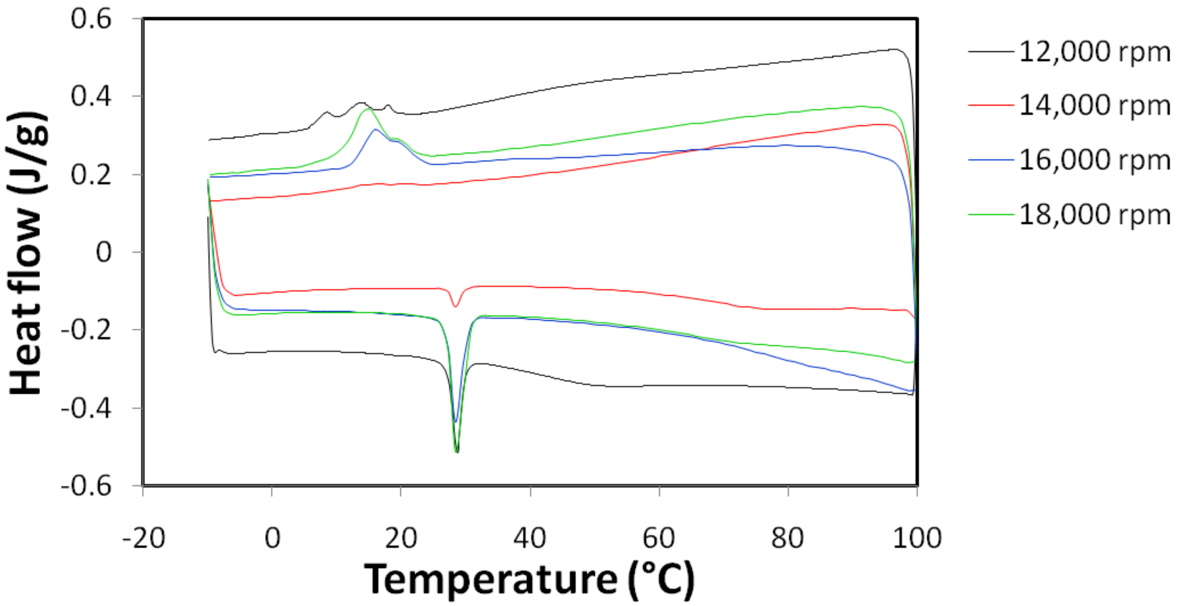


Figure A.6 The DSC the microcapsules which sprepared at the mole ratio of Tween 20 : PCMs which is 0.5:1, The content of the phase change material which is 50% and the various homogenizing speed.

VITA

Miss Phaiphan Saowapa was born on March 5, 1986 in Buriram Province, Thailand. She received the Bachelor Degree of Chemical Technology from Faculty of Science, Chulalongkorn University in 2008. She studies the Master degree at Chulalongkorn University in June, 2010.

LIST OF PUBLICATIONS.

1. Phaiphan Saowapa, Wiyong Kangwansupamonkon and Apinan Soottitanawat. “Microencapsulation of n-Octadecane with Silica from Sodium Silicate by Spray Drying Process”. Pure and Applied Chemistry International Conference (PACCON2012), Chiangmai, January 11-13, 2012.