การกักเก็บวัสดุแบบเปลี่ยนเฟสเพื่อการประยุกต์ในยางธรรมชาติ

นายทรงพล ผดุงพัฒนากูล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2554
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

ENCAPSULATION OF PHASE CHANGE MATERIAL FOR APPLICATION IN
NATURAL RUBBER

Mr. Songpon Phadungphatthanakoon

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2010

Thesis title   ENCAPSULATION OF PHASE CHANGE
                      MATERIAL FOR APPLICATION IN
                      NATURAL RUBBER
By   Mr. Songpon Phadungphatthanakoon
Field of Study   Chemistry
Thesis Advisor   Associate Professor Supason Wanichwecharungruang, Ph.D.
Thesis Co-advisor   Assistant Professor Sirilux Poompradub, Ph.D.

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

………………………………………..Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITEE

....Chairman

(Assistant Professor Warinthorn Chavasiri, Ph.D.)

....Thesis Advisor

(Associate Professor Supason Wanichwecharungruang, Ph.D.)

....Thesis Co-advisor

(Assistant Professor Sirilux Poompradub, Ph.D.)

………………………………………..Examiner

(Assistant Professor Sumrit Wacharasindhu, Ph.D.)

………………………………………..External Examiner

(Thitinun Karpkrid, Ph.D.)

ทรงพล ผดุงพัฒนากูล : การกักเก็บวัสดุแบบเปลี่ยนเฟสเพื่อการประยุกต์ในยางธรรมชาติ (ENCAPSULATION OF PHASE CHANGE MATERIAL FOR APPLICATION IN NATURAL RUBBER) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ศุภศร วนิชเวชารุ่งเรือง, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม ผศ.ดร.ศิริลักษณ์ พุ่มประดับ, 71 หน้า.

วัสดุแบบเปลี่ยนเฟส (PCM) เป็นระบบการกักเก็บพลังงานในรูปความร้อนแฝงที่สามารถเก็บความร้อน จึงช่วยควบคุมให้อุณหภูมิคงที่ได้ นอร์มัลไอโคแซน (N – eicosane) และ พาราฟิน มีอุณหภูมิการเปลี่ยนเฟสในช่วงใกล้เคียงกับอุณหภูมิของร่างกายมนุษย์ และมีความหนาแน่นในการเก็บพลังงานที่โดดเด่น จึงเป็นที่นิยมมากสำหรับการใช้งานที่เกี่ยวข้องกับการควบคุมอุณหภูมิวัสดุให้ใกล้เคียงอุณหภูมิของร่างกายมนุษย์ เช่นวัสดุก่อสร้าง สิ่งทอ และเฟอร์นิเจอร์ ในงานวิจัยนี้แสดงให้เห็นถึงการใช้กระบวนการใหม่ที่สามารถกักเก็บนอร์มัลไอโคแซนและพาราฟิน ภายในเปลือกพอลิเมอร์ผสมของเอทิลเซลลูโลสและเมทิลเซลลูโลส เพื่อการแก้ปัญหาเกี่ยวกับการรั่วไหลของนอร์มัลไอโคแซนและพาราฟินระหว่างการเปลี่ยนสถานะเป็นของเหลว การเข้ากันไม่ได้กับวัสดุที่มีขั้ว และความไม่มีเสถียรภาพทางเคมีของนอร์มัลไอโคแซนและพาราฟิน กระบวนการกักเก็บนี้สามารถกักเก็บนอร์มัลไอโคแซนและพาราฟินไว้ภายในเปลือกพอลิเมอร์ผสมของ เอทิลเซลลูโลสและเมทิลเซลลูโลสได้ดี ซึ่งทำให้ได้อนุภาคทรงกลมที่มีขนาดในหน่วยไมโครเมตร ที่สามารถกระจายตัวในน้ำได้ดีและมีค่าความจุความร้อนที่ดี นอกจากนี้อนุภาคนอร์มอลไอโคแซนที่ได้ ยังให้ค่าความจุความร้อนที่เพิ่มขึ้นเมื่อเปรียบเทียบกับนอร์มอลไอโคแซนบริสุทธิ์ นอกจากนี้การผสมอนุภาคของนอร์มอลไอโคแซนที่สามารถกระจายตัวในน้ำลงในน้ำยางธรรมชาติ พบว่าอนุภาคสามารถกระจายตัวได้ดีในเนื้อยาง และพบว่านอกจากยางที่ได้จะมีความสามารถในการควบคุมอุณหภูมิแล้วสมบัติเชิงกลของยางยังดีขึ้นด้วย

ภาควิชา.....................เคมี.............. ลายมือชื่อนิสิต...

สาขาวิชา...................เคมี.............. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก…….....……….............

ปีการศึกษา…...........2554……….. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม…….....……….............

5272319723 : MAJOR CHEMISTRY

KEYWORDS : PHASE CHANGE MATERIAL, MICROENCAPSULATION, ENERGY STORAGE, CRYSTALLIZATION, LATENT

SONGPON PHADUNGPHATTHANAKOON: ENCAPSULATION OF PHASE CHANGE MATERIAL FOR APPLICATION IN NATURAL RUBBER. ADVISOR: ASSOC. PROF. SUPASON WANICHWECHARUNGRUANG, Ph. D., CO ADVISOR: ASST. PROF. SIRILUX POOMPRADUB, Ph. D., 71 pp.

Phase change material (PCM) is the latent heat storage system that can store heat approximately isothermally within a very narrow temperature range. N-eicosane and parafin possess phase change temperature in the range of human comfort with outstanding energy storage density, thus they are very popular for applications involving temperature regulation for human comfort such as building materials, thermoregulated fabrics and furniture. Here we demonstrated the use of a novel microencapsulation process to encapsulate n-eicosane (C20) and paraffin into the blend of ethylcellulose (EC) and methylcellulose (MC) to solve the problems on leakage during the melted state, incompatible with polar materials and chemical instability of the the two PCMs. Both PCMs could be encapsulated into the EC/MC shell and the obtained microspheres showed good water dispersibility and good latent heat storage capacity. Very interstingly, N-eicosane microspheres showed increased heat storage capacity comparing to the unencapsulated N-eicosane. Blending of the water dispersible n-eicosane microspheres into natural rubber latex showed excellent compatibility, and the obtained rubber showed not only obvious thermo-regulation property but also improved mechanical property.

Department :…..CHEMISTRY……………. Student's Signature……………………………...

Field of Study :……… CHEMISTRY………. Advisor's Signature…………………………….

Academic Year : ……. 2011…………… … Co- advisor's Signature………………………....

ACKNOWLEDGEMENTS

CONTENTS

LIST OF TABLES

Table   **Page**

LIST OF FIGURES

Figure Page

Figure **Page**

LIST OF SCHEMES

LIST OF ABBREVIATIONS

δ	chemical shift
°C	degree Celsius
DG	degree of grafting
DS	degree of substitution
g	gram (s)
Hz	hertz
h	hour
IR	Infrared
μg	microgram (s)
mg	milligram (s)
mL	milliliter (s)
mV	millivolt
mW	milliwatt
min	minute (s)
MW	molecular weight
nm	nanometer (s)
NMR	nuclear magnetic resonance
ppm	parts per million
%	percent
cm^{-1}	per centimeter (s)
SEM	Scanning electron microscope
N-SCS	*N*-succinylchitosan
TEM	Transmission electron microscope
UV	ultraviolet
cm^{-1}	unit of wavenumber (IR)
λ	wavelength

CHAPTER I

INTRODUCTION

1.1 Phase change material (PCM)

Phase change material (PCM) is the latent heat storage system that can store heat approximately isothermally within a very narrow temperature range. PCM can change status between the solid and liquid. When the temperature is above the melting point, PCMs liquefy and absorb and store heat, thus cooling the surrounding temperature. On the other hand, when the temperature is below the melting point, PCMs solidify and release heat, thus warming the surrounding temperature. In recent years due to increasing energy consumption, PCM has been studied and used to control and manage heat transfer in many applications including thermoregulated building materials [1], heat and solar energy storage devices and thermoregulated fabric [2]. Recently, application of PCM in the sport wears, and the clothing textiles is well-known. PCM-microcapsules have been incorporated into textile structures. In 2004, Ulfvengren [3] developed a cooling vest for athletes for reducing body temperature. PCMs have also been proposed for cooling a newborn baby [4] Phase change technologies can also be used for cryosurgery, which is a technique for destroying the unwanted cell by freezeing and thawing [5]

Working principle of PCM. When a material converts from one state to another state, this process is called phase change, such as solid to liquid, liquid to gas, solid to gas and solid to solid. Heat absorbed or released during the phase change process is called latent heat. PCM which can change from solid to liquid or from liquid to solid state at desired temperature can generally be used as latent heat storage material. The phase change from solid to liquid occurs when the melting temperature of PCM is reached. Because PCM absorbs large quantities of energy from the surrounding, the ambient temperature decreases. In the opposite way PCM releases large quantities of heat storage energy from itself to surrounding area during the solidification process. This makes the ambient temperature increase.

1.2 Classes of materials

The organic and inorganic materials are used PCMs. More than 500 natural PCMs, and synthetic PCMs are known [6] which depend on molecular effects.

1.2.1 Inorganic materials

The inorganic materials cover a wide temperature range when compared with the organic materials. Inorganic materials used as PCM include hydrated inorganic salt with 'n' water molecules (Table 1.1)

Advantages. Low cost and abundant of salt hydrate make them attractive for heat storage applications [7] Materials in this group usually possess sharp melting point, high heat of fusion, and high thermal conductivity when compared with other PCMs.

Disadvantages. Segregation, a formation of other hydrate or dehydrated salt, usually occurs with many salt hydrates. Salt hydrate show the super-cooling because it does not start to crystallize at the freezing point of other PCMs. Salt hydrate causes the corrosion in the metal containers.

Table 1.1 Examples of salt hydrates that have been investigated as PCM

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)
$LiClO_3·3H_2O$	8	155	- -	1530 (liquid) 1720 (solid)
$KF·3H_2O$	18.5	231	- -	1447 (liquid, 20°C) 1455 (solid, 18°C)
$CaCl_2·6H_2O$	29, 30	171, 190	0.540 (liquid) 1.088 (solid)	1562 (liquid, 32°C) 1710 (solid, 25°C)
$LiNO_3·3H_2O$	30	296	- -	- -
$Na_2SO_4·10H_2O$	32	254	- 0.554	- 1485 (solid)
$Na_2HPO_4·12H_2O$	35-44	280	0.476 (liquid) 0.514 (solid)	1442 (liquid) 1522 (solid)
$Na_2S_2O_3·5H_2O$	48-55	187, 209	- -	1670 (liquid) 1750 (solid)
$MgCl_2·6 H_2O$	117	165, 169	0.570 (liquid) 0.704 (solid°C)	1450 (liquid,120°C) 1569 (solid, 20 °C)

1.2.2 Organic materials

Popular organic materials used as PCM include paraffins, fatty acids, and sugar alcohols. They covered the temperature range between 0 ºC to approximately 200 ºC. The generally used organic PCMs are alkane, with the general formula of C_nH_{2n+2} (Figure 1.1). These materials are non-toxic, inexpensive, and harmless to the environment. Examples of alkene that have been investigated as PCM, are presented in Table 1.2. The melting point of *N*-eicosane is near the human body temperature. *N*-Eicosane is chosen for PCMs in the thermo-regulated textiles and clothing in order to control human body temperature. In this research, *N*-eicosane and paraffin were used as core material for PCM encapsulation.
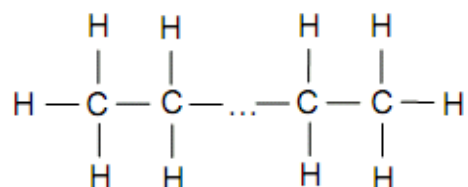
Figure 1.1 Chemical structure of linear alkanes.

Advantages. Alkanes are chemical stabilities and they show high heats of fusion. Alkanes are safe and non-reactive [8-9]. They are compatible with all metal containers and easy to incorporate into the heat storage systems [10].

Disadvantages. The thermal conductivity is low. Alkanes are flammable, but this can be easily alleviated by a proper container [11].

Table 1.2 Examples of alkene that have been investigated as PCM.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)
n-Hexadecane C$_{16}$H$_{34}$	18	210, 238	- 0.21 (solid)	760 (liquid,20°C) -
n-Heptadecane C$_{17}$H$_{36}$	19	240	- -	776 (liquid,20°C) -
n-Octadecane C$_{18}$H$_{38}$	28	200, 245	0.148 (liquid,40°C) 0.358 (solid, 25 °C)	774 (liquid,70°C) 814 (solid,20 °C)
n-Eicosane C$_{20}$H$_{42}$	38	283	- -	779 -
n-Triacontane C$_{30}$H$_{62}$	66	-	- -	775 -
n-Tetracontane C$_{40}$H$_{82}$	82	-	- -	- -
n-Pentacontane C$_{50}$H$_{102}$	95	-	- -	779 -
Polyethylene C$_n$H$_{2n+2}$ n up to 100000	110-135	200	- -	- 870-940

Fatty acidgeneral formula is $CH_3(CH_2)_{2n}COOH$ (Figure 1.2). Tables 1.3 show the examples of fatty acids that have been investigated as PCM.
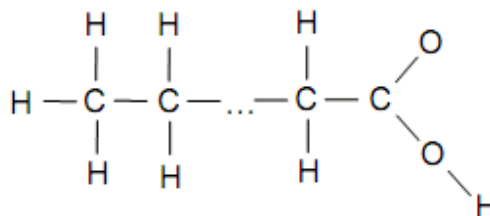
Figure 1.2 Chemical structure of fatty acids.

Table 1.3 Examples of fatty acids that have been investigated as PCM.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
Caprylic acid $CH_3(CH_2)_6COOH$	16	149	0.149 (liquid, 38°C) -	901 (liquid, 30 °C) 981 (solid, 13 °C)
Capric acid $CH_3(CH_2)_8COOH$	32	153	0.149 (liquid, 40°C) -	886 (liquid,40°C), 1004 (solid, 24°C)
Lauric acid $CH_3(CH_2)_{10}COOH$	42-44	178	0.147 (liquid, 50°C) -	870 (liquid, 50°C), 1007 (solid, 24°C)
Myristic acid $CH_3(CH_2)_{12}COOH$	56	186, 204	- 0.17 (solid)	861 (liquid, 55°C), 990 (solid, 24 °C)
Palmitic acid $CH_3(CH_2)_{14}COOH$	61, 64	185, 203	- -	850 (liquid, 65 °C 989 (solid, 24 °C)

Sugar alcohols are a hydrogenated form of a carbohydrate. The general formula is HOCH$_2$[CH(OH)]$_n$CH$_2$OH, (Figure 1.3). Examples of sugar alcohols that have been investigated as PCM, are presented in Table 1.4.
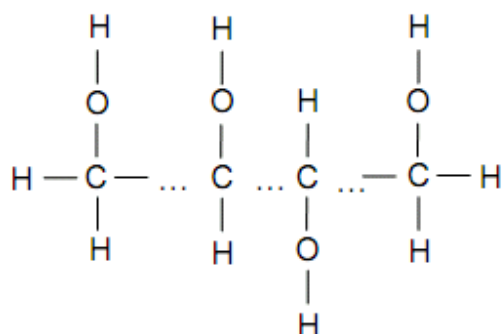
Figure 1.3 Chemical structure of sugar alcohols.

Table 1.4 Examples of sugar alcohols that have been investigated as PCM.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
D-Sorbitol C$_6$H$_8$ (OH)$_6$	97	185	- -	- 1520 (solid, 20°C)
Erythritol C$_4$H$_6$ (OH)$_4$	120	340	0.326 (liquid,140°C), 0.733 (solid, 20 °C	1300(liquid,140°C), 1480 (solid, 20 °C)
D-Mannitol C$_6$H$_8$ (OH)$_6$	167	316	- -	- 1520 (solid, 20 °C)
Galactitol C$_6$H$_8$ (OH)$_6$	188	351	- -	- 1520 (solid, 20 °C)

Polyethylene glycol, or PEG, is a polymer with the general formula $C_{2n}H_{4n+2}O_{n+1}$. The repeating unit of PEG is oxyethylene ($-O-CH_2-CH_2-)_n$ (Figure 1.4). The melting temperature of PEG depends on the molecular weight of polymer. The examples of PEG that have been investigated as PCM, are presented in Table 1.5.

Figure 1.4 Chemical structure of polyethylene glycols.
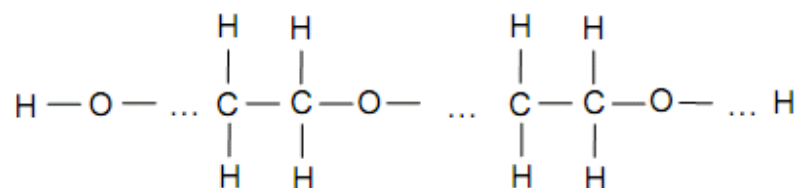
Table 1.5 Examples of PEGs and some of their properties.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
Diethylene glycol $C_4H_{10}O_3$	-10 to -7	-	-	1120 (liquid,20°C)
			-	-
Triethylene glycol $C_6H_14O_4$	-7	-	-	1120 (liquid,20°C)
			-	-
PEG400	8	100	0.19 (liquid, 38 °C)	1125 (liquid,25°C),
			-	1228 (solid, 3 °C)
PEG600	17- 22	127	0.19 (liquid, 38 °C)	1126 (liquid,25°C),
			-	1232 (solid, 4 °C)
PEG1000	35 - 40	-	-	-
			-	-
PEG3000	52 - 56	-	-	-
			-	-
PEG6000	55 - 60, 66	190	-	1085 (liquid,70°C),
			-	1212 (solid, 25 °C)
PEG10000	55 - 60	-	-	-
			-	-

1.3 The encapsulation of PCM

Encapsulation of PCM it is normally required to 1) avoid the contact of PCM with the environment, which might harm the environment or change the composition of the PCM, 2) improve heat transfer to the surrounding through a better contact between the capsules and the environment, 3) improve in cycling stability and mechanical stability and 4) prevent PCM leakage during the melting stage.

Encapsulations are usually classified by their sizes into macro- and microencapsulation. Microencapsulation is the packaging of micronized materials in the shape of capsules with approximately 10–50 µm in diameter (Fig 1.5). The wall material of the capsule can be formulated by using a wide variety of materials including natural and synthetic polymers.
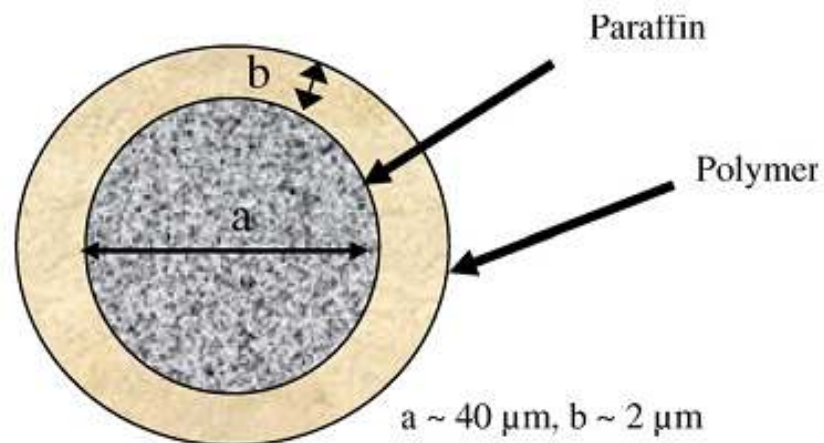
Figure 1.5. Microencapsulation: Paraffin core material with a hard polymeric shell.

Mechanical stability

Composition of PCM and the other material is a mechanically stable structure. It is called the shape-stabilized PCM. Independent of the phase of the PCM, solid or liquid, the shape is maintained by the supporting structure.

Thermal conductivity

All non-metallic liquids, including PCM possess low thermal conductivity, thus causing the low heat exchange rate between the PCM and environment. One possibility to increase the thermal conductivity of the PCM is to add materials with larger thermal

conductivity into the system. Therefore, thermal conductivity enhancer would be useful in many PCM applications [12] The thermal conductivities of PCM can be enhanced by adding metal filler, carbon nanofiber/fiber fillers etc [12–15] into the blend and usually carbon fibers are strong resistance to corrosion.

Examples of microencapsulation

Today microencapsulation of PCM is technical possibility for organic PCM materials. The commercial products seem to use exclusive paraffins. Fig.1.6 shows commercial paraffin-microcapsules, their diameters are 2-20 μm ranges, produced by the company BASF.
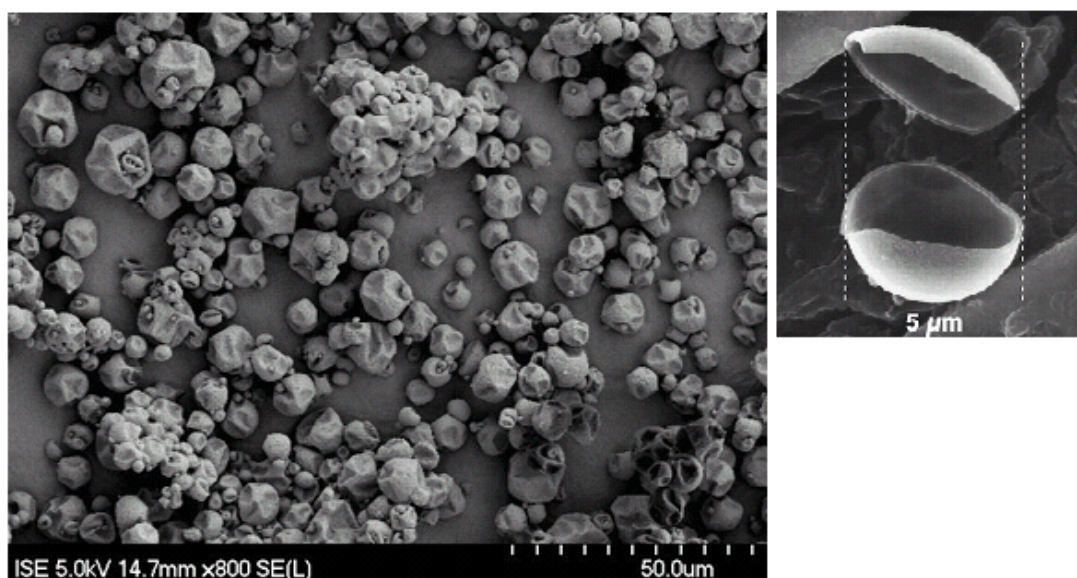
Figure 1.6 Electron microscope images of many capsules and an opened microcapsule.

The microencapsulated PCM is available as fluid dispersion or as dried powder (Fig.1.7).
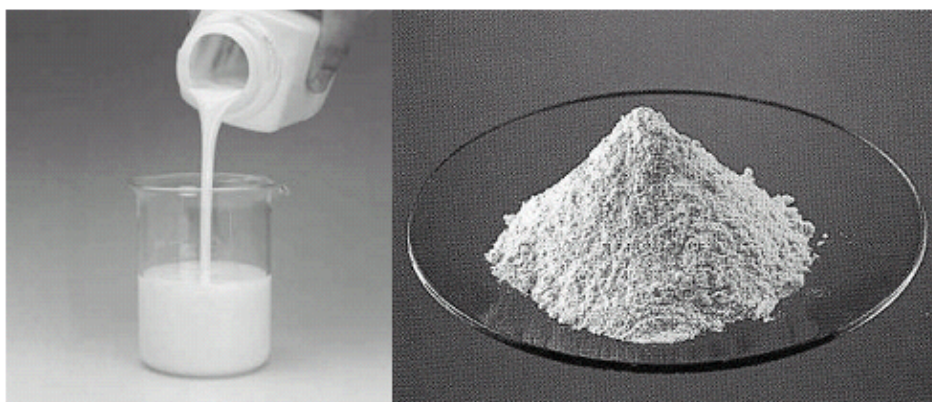
Figure 1.7 Microencapsulated paraffin produced by BASF, on the left as fluid dispersion, and on the right as dry powder.

Amphiphilic polymers are interesting to be used as polymer wall because they can entrap hydrophobic molecules. Their loading capacity properties depend on the matching of the loaded hydrophobic core and polymer. In this research, ethyl cellulose, methyl cellulose, and *N*-succinylchitosan are experimented as shell material for *N*-eicosane and paraffin encapsulation.

Ethyl cellulose (EC)
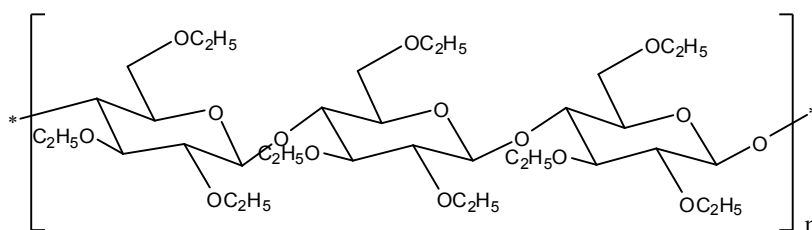
Figure 1.8.Structure of ethyl cellulose

Ethyl cellulose (EC) is a cellulose derivative which some of the hydroxyl groups on the repeating glucose units are converted into ethyl ether groups. It is used mostly in pharmaceutical industry as drug binder such as thin-film coating material, and in food industry as a food additive and a. Ethyl cellulose is the most stable cellulose derivatives. It is resistant to alkalis but sensitive to acids. Ethyl cellulose takes up little water from

moist air or during immersion, and water evaporation leaves the ethyl cellulose with unchanged property. Light such as the visible and ultraviolet radiant do not discolor Ethyl cellulose. The glass-transition temperature of ethyl cellulose is 140 °C [16] Ethylcellulose is non-toxic and biocompatible [17].

Methyl cellulose (MC)

Methyl cellulose (MC) is a cellulose derivative which some of the hydroxyl groups on the repeating glucose units are converted into methyl ether groups. It is a hydrophilic polymer and it dissolves in water as the clear viscous solution or gel. It is sold under a variety of trade names and it is used as the thickener and emulsifier in various food and cosmetic products. It is not toxic and not allergenic [18].
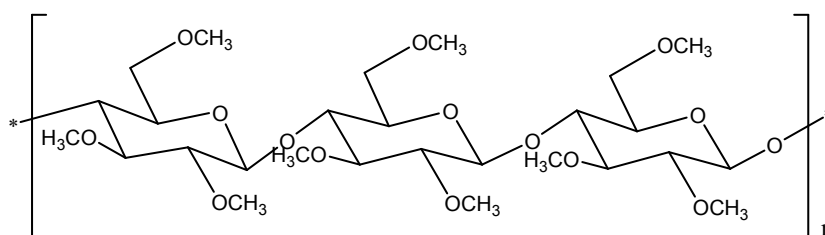
Figure 1.9 Structure of methyl cellulose

Chitosan

The chemical structure in chitosan or alpha-(1-4)-amino-2-deoxy-beta-D-glucan is similar to glycosaminoglycans. Chitosan is a derivative of chitin, a natural polysaccharide found in the shells of crustaceans such as crabs and shrimps. It is polycationic biopolymer which generally obtained by alkaline deacetylation of chitin (Figure 1.10). Chitosan is insoluble in water, but it dissolves in the aqueous solutions of organic acids such as acetic, formic, citric, and inorganic acids such as diluted hydrochloric acid. Chitosan is biocompatible and possesses anti-microbial activity [19-22]
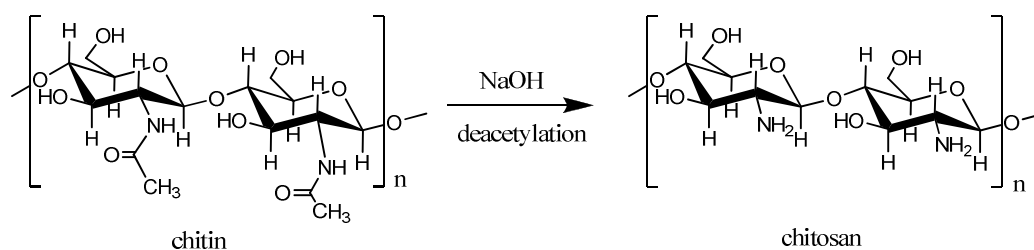
Figure 1.10 Deacetylation of chitin

Chemical modification of Chitosan

The structure of chitosan is widely modified in order to improve its solubility and applications [22-24] *N*-succinyl-chitosan, a water dispersible chitosan derivative (Figure 1.11) was investigated in this research.
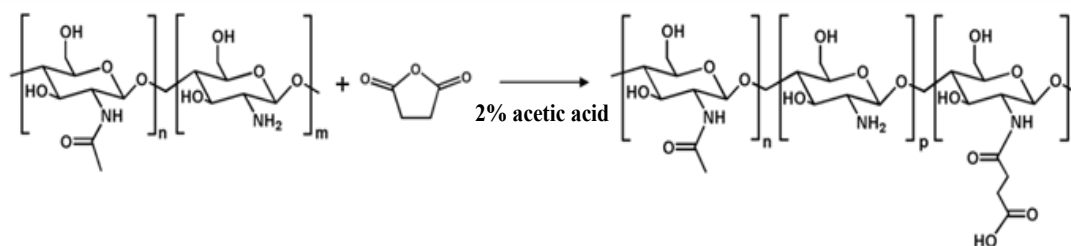
Figure 1.11 Preparation of *N*-succinylchitosan

1.4 Natural rubber

Natural rubber (NR) is one of the most important commodities of Thailand, Thailand has become the world's largest producer and exporter of natural rubber since 1991.   This research also involves the development of natural rubber with thermo-regulation property via the use of the novel encapsulated PCM, also developed in this project.

NR is an unsatulateted elastomer with excellent mechanical properties. It is isolated from the *Hevea brasiliensis tree* However, NR has poor resistance to oxidation and organic solvent. NR is a hydrocarbon polymer of isoprene (methylbuta-1, 3-diene) (Figure 1.11) with the *cis*- configuration of ethylene. In other words, natural rubber (NR) contains 93–95% cis-1, 4-polyisoprene.
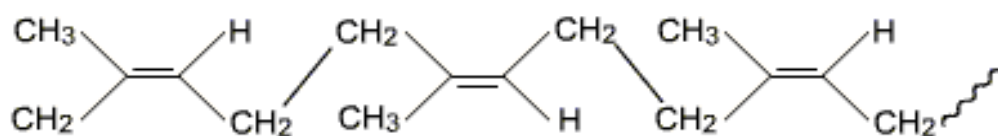
trans-Polyisoprene
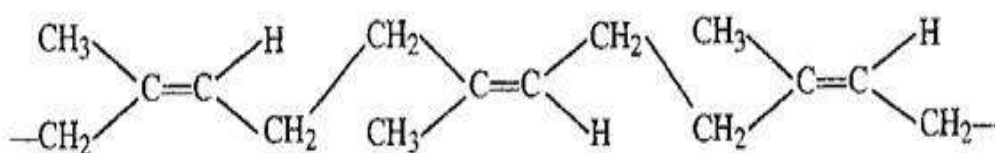
cis-Polyisoprene

Figure 1.12 *Cis* and *trans* isomers of natural rubber

NR latex is a white liquid; similar to milk with a pH of 6.5–7.0 and a density of 0.98 g cm^{-3}. Fresh NR latex has the dry rubber content (DRC) of about 25-40% and 5-10% non rubber substances. The non rubber components are proteins, carbohydrates, lipid, and inorganic salt. The traditional preservative is concentrated ammonia solution; ammonia is added in small quantities to the latex collected from the cup. The compositions of fresh NR latex are shown in Table 1.6 [25-26].

Table 1.6 Composition of fresh natural rubber latex

Composition	Content (% by weight)
Totol solid content	36
Dry rubber	33
Proteinous substance	1.0-1.5
Resinous substance	1.0-2.5
Carbohydrates	1.0
Inorganic matter	Up to 1.0
Water	60

Latex concentrate is used as a raw material for many dipped products such as gloves, furniture, etc.

1.5 Literature reviews of PCM

New PCM innovation

In 2002, Cabeza *et al*. [27] reported that the PCM could be used for transporting temperature sensitive medications and food because of the PCM's capability to stabilize the temperature for a range of several degrees. Several companies are engaged in the research of using PCMs to transport temperature sensitive products [237 - 241].

In 2000, Vasiliev *et al*. [28] developed the latent heat storage module for motor vehicles so the heat is stored when the engine is stopped, and can be used to preheat the engine on a new start. It is possible to reach an optimized working temperature within the engine in a much shorter time using heat storage comparing to without heat storage.

In 2004, Tan *et al*. [29] conducted an experimental study on the cooling of mobile electronic devices, such as personal digital assistants (PDAs) and wearable computers, using a heat storage unit (HSU) filled with the phase change material (PCM) of n-eicosane inside the device. The high latent heat of n-eicosane in the HSU absorbs the heat dissipation from the chips and can maintain the chip temperature below the allowable service temperature of 50 °C for 2 h of transient operations of the PDA.

In 2004, Koschenz *et al*. [30] developed a thermally activated lightweight ceiling panel for retrofitted buildings. It was demonstrated, by means of simulation calculations and laboratory tests, that a 5 cm layer of microencapsulated PCM (25% by weight) and gypsum surface will maintain a comfortable room temperature in standard office buildings. Hexadecane was tried as a PCM in this prototype set-up.

In 2005, Zhang *et al*. [31] fabricated microencapsulated n-alkanes (n-octadecane, n-nonadecane, and n-eicosane) by in situ polymerization using urea–melamine–formaldehyde polymer as shells in order to study crystallization and prevention of supercooling of microencapsulated n-alkanes. The X-ray diffraction results showed that the crystal system of the n-alkane in the microcapsule was the same as that of the bulk. The enthalpies of the microcapsules containing approximately 70 wt% n-alkanes were approximately 160 J/g. The melting temperatures of the microencapsulated n-alkanes were the same as those of the bulk. There were multiple peaks on the DSC cooling curves that could be attributed to liquid–rotator, rotator–crystal, and liquid–crystal transitions. The DSC cooling curves of microencapsulated n-octadecane were affected by the average diameters. The maximum degree of supercooling of microencapsulated n-octadecane was approximately 26.0 ◦C at a heating and cooling rate of 10.0 ◦C/min. Supercooling causes the latent heat to be released at a lower temperature, which is disadvantageous for the energy storage application. Adding 10.0 wt% of 1-octadecanol inside the microcapsules as a nucleating agent decreased the degree of supercooling of microencapsulated n-octadecane from 26 ◦C to approximately 12 ◦C at a heating and cooling rate of 10.0 ºC/min.

In 2009, Wang *et al.* [32] prepared a novel shape-stabilized composite of PEG and silicon dioxide. PEG and SiO_2 were chosen as phase change material and supporting material, respectively. Because of the effect of capillary force and surface tension force, there was no leakage of liquid PEG from the porous of SiO2 network. The maximum weight percentage for PEG dispersed in the PCM composites without any leakage of the melted PEG was as high as 85%.The PEG (85%)/SiO2 composite had a large enthalpy of 162.9 J/g and suitable melting temperature (Tm = 61.61 $^\circ$C).

In 2009, Fang *et al*. [33] fabricated nanocapsule of phase change material by using in situ polymerization methods. *N*-Tetradecane was used as the core material. Urea and formaldehyde were used for the shell polymerization. The morphology of the nanocapsules observed by a scanning electronic microscope (Figure 1.13.), indicated that the nanocapsules had general size of about 100 nm and the core material was well encapsulated. DSC analysis indicated that the mass content of n-tetradecane was up to 60%, which resulted in a high latent heat of fusion at 134.16 kJ/kg.
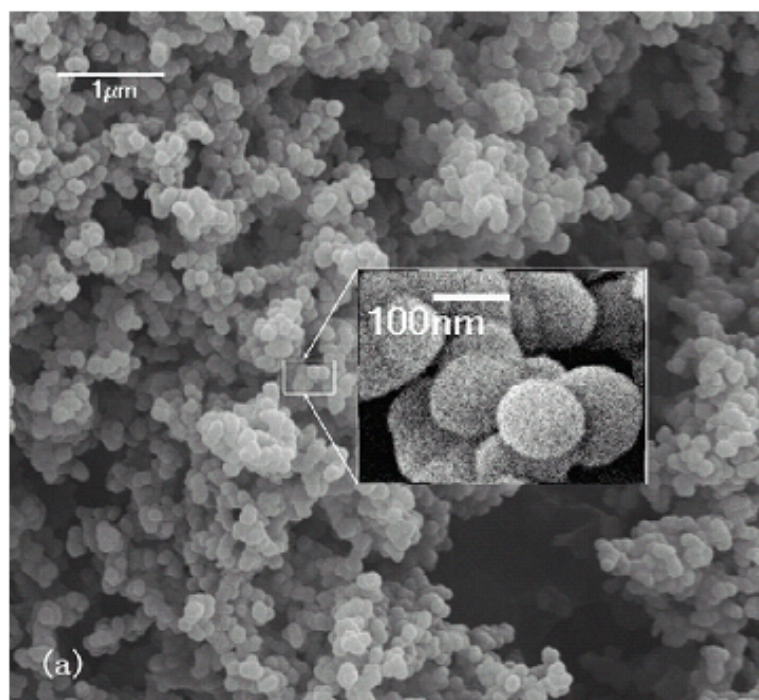
Figure 1.13 SEM photos of nanocapsules.

Use of *N*-Eicosane as PCM

In 2009, Deveci *et al.* [34] fabricated PCM microcapsules with reasonable size and encapsulation efficiency by complex coacervation of chitosan and silk fibroin. Results showed that microcapsules produced by the coacervation process had a spherical shape. Microcapsules obtained at a relatively low silk fibroin/ chitosan ratio of 5 had a dense, homogeneous, and nonporous wall. At relatively high silk fibroin/ chitosan ratio of 20, in the other hand, microcapsules had an inner layer with a smoother surface and a rough outer surface with a sponge-like appearance. It is possible that the extra layer improves the mechanical strength of capsule wall. In terms of microcapsule size and encapsulation efficiency, silk fibroin/ chitosan polymer ratio had the strongest influence. At the high silk fibroin/ chitosan ratio, both microencapsulation efficiency and microcapsule size increased. The *N*-Eicosane content affected microencapsulation efficiency as well. A high n-icosane content improved microencapsulation efficiency particularly at higher silk fibroin/ chitosan ratios. A raise in cross-linking agent content had a positive effect on microencapsulation efficiency and microcapsule size at low n-icosane contents. This study confirms that the silk fibroin/ chitosan wall system can be utilized to encapsulate a phase change material

In 2011, Alkan *et al.* [35] prepared PMMA microcapsules containing *N*-Eicosane by emulsion stirring at 2000 rpm. The PMMA microcapsules possessed average diameter of 0.7 µm. The SEM results indicated that the PMMA/eicosane microcapsules were successfully prepared by emulsion polymerization and they possessed smooth and compact surface. The temperatures and latent heats of melting and crystallization of microcapsules were determined using DSC analysis method. Thermal properties evaluated from the curves indicate that the microcapsules melt at 35.2 ± 0.12 °C, crystallize at 34.9 ± 0.15 °C while pure *N*-eicosane has a melting point of 34.6 ± 0.09 °C and crystallization point of 33.4 ± 0.13 °C. Latent heats of melting and freezing of the microcapsules were found to be 84.2 ± 1.12 J/g and 87.5 ± 1.35 J/g, respectively, while latent heats of melting and freezing of pure *N*-eicosane were found to be 242.8 J/g and 244.6 J/g respectively. The encapsulation ratio of n-eicosane was calculated to be 35 wt%. The PMMA/eicosane microcapsules were stable for 5000 rounds of thermal cycling

test. The latent heats of melting and crystallization of the microcapsules after repeated 5000 thermal cycling were measured as 99.1 ± 1.72 J/g and 102.9 ± 1.31 J/g, respectively. There was no significant temperature or enthalpy change of latent heat storage capacity after thermal cycling. The chemical stability of PMMA/eicosane microcapsules after repeated thermal cyclings was also investigated by FT-IR analysis. The peak positions were consistent in the samples before and after thermal cyclings, indicating that chemical structure of microcapsules was not affected by thermal cyclings. This means that no chemical degradation of PMMA/eicosane occurred during thermal cyclings.

In 2010, Sarl *et al.* [36] prepared PMMA/heptadecane microcapsules by emulsion polymerization technique. SEM analyses showed that the microcapsules had smooth and spherical shape with average diameter of 0.26 μm (Figure 1.14). The temperatures of melting and freezing and latent heats of melting and freezing of the PMMA/heptadecane microcapsules were determined as 18.2 and 18.4 °C and 81.5 and 84.2 J/g, respectively. The ratio of the heptadecane in the PMMA microcapsules was 38 wt. %. Thermal cycling test showed that the microPCMs had good thermal reliability after 5000 melting and freezing cycling.
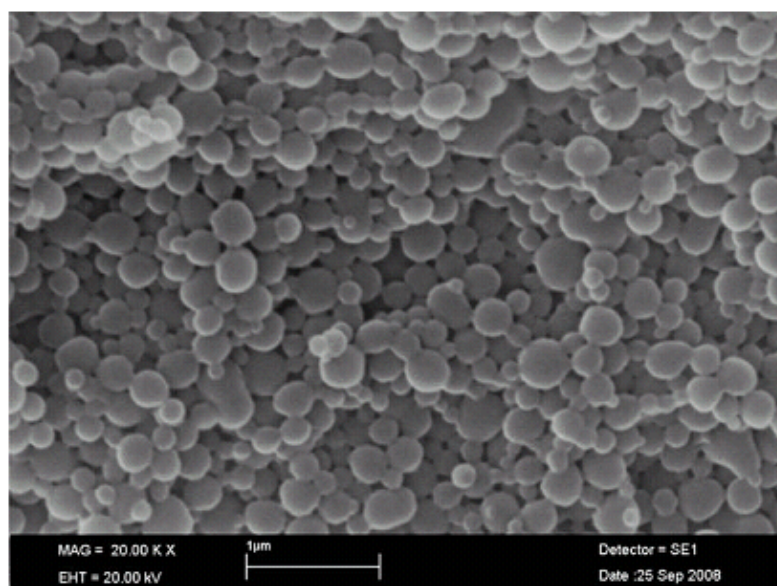
Figure 1.14 SEM image of PMMA/heptadecane microcapsules.

In 2010, Sanchez *et al.* [37] prepared polystyrene microcapsules containing paraffin wax. Fabric coated with 35% of microcapsules was capable of absorbing 7.6 J/g of heat. A thermoregulatory effect of 8.8, 6.3, 5.6 and 2.5 ºC after 6, 12, 44 and 75 s, respectively, was observed by means of infrared thermography (Figure 1.15).
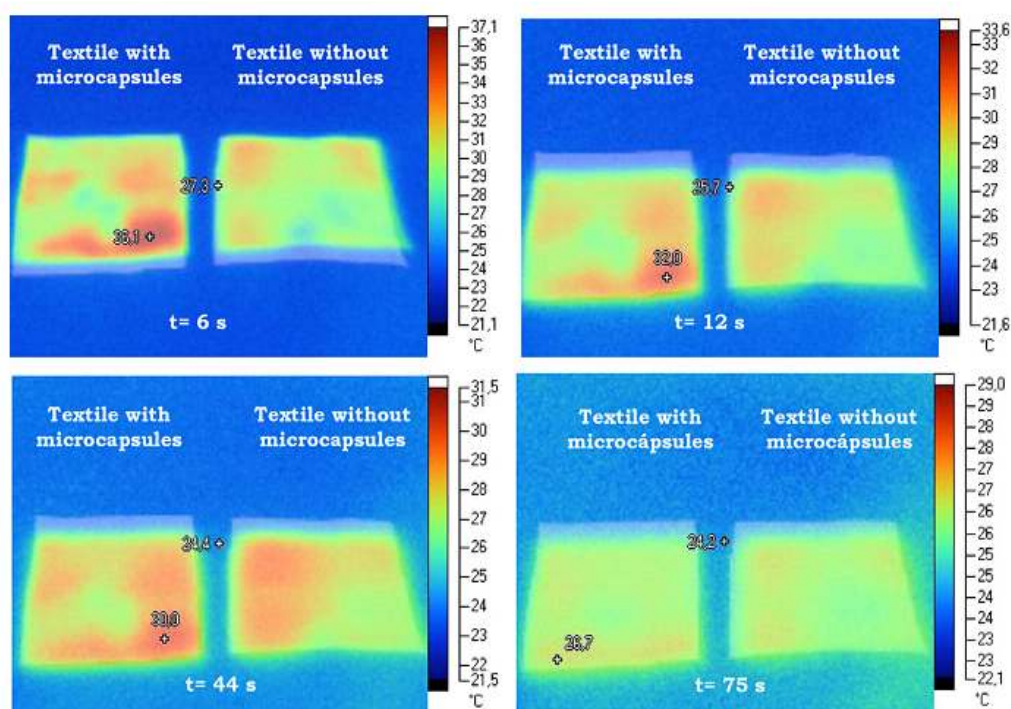
Figure 1.15 Comparison of thermal images obtained for SUPERMOR-35 and a normal textile preheated at different times.

Research goals

The aim of this research is to prepare the phase change microcapsule using biocompatible/non-toxic polymer. *N*-Eicosane and paraffin molecules were used as PCM. The obtained PCM-microcapsule was also used in fabricating thermoregulated NR.

CHAPTER II

EXPERIMENTAL

2.1 Materials and Chemicals

Ethylcellulose (EC) and methylcellulose (MC) were purchased from Sigma-Aldrich (St. Louis, Mo, USA). Chitosan powder with approximately 85% degree of deacetylation and 30,000 Da of viscosity-average molecular weight was purchased from Seafresh Chitosan (Lab) Co., Ltd (Bangkok, Thailand). Succinic anhydride was purchased from Acros organics (Geel, Belgium). *N*-eicosane (C20) 99% was from Acros organics (Geel, Belgium). Dialysis membranes with a molecular weight cut off of 12000-14000 Daltons (size 76 mm. × 49 mm) were purchased from Aldrich Chemical Company (Steinheim, Germany). Natural rubber (60 DRC) (Thai Rubber Latex Corporation, Bangkok, Thailand)

2.2 Encapsulation of *N*-eicosane

2.2.1 Chitosan shell

Preparation of *N*-succinylchitosan (NSCS)
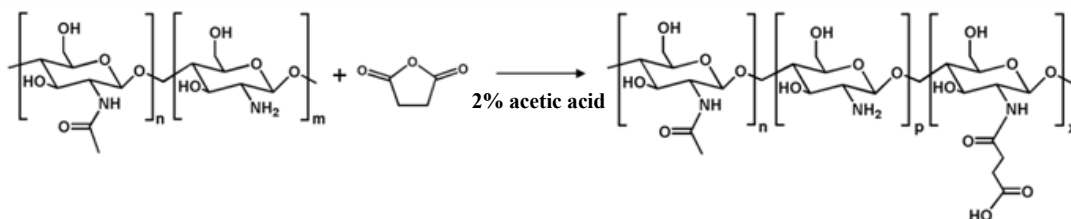
Scheme 2.1. Preparation of *N*-succinylchitosan.

N-succinylchitosan (N-SCS) was prepared according Scheme 2.1. This experiment was carried out at chitosan to succinic anhydride mole ratios, 2:1, 4:1. For each mole ratios, 1 g of chitosan (6.25 mmole) was dissolved in 50 mL of 2 % v/v acetic acid. The 0.3125 and 0.156 g of succinic anhydride (3.125 and 1.562 mmoles, respectively) in 10 mL of acetone were slowly dropped into chitosan solution. Then the solution was stirred for 12 hours at room temperature and precipitated by excess acetone. The precipitate was collected by filtration and washed with acetone several times. Finally, a yellow powder was obtained. The product was characterized by Nuclear magnetic resonance (NMR), a Varian mercury spectrometer (Variance Inc., Palo Alto, USA), operating at 400 MHz.

N-succinylchitosan (N-SCS 1): 70% yields of yellow powder and 0.43 degree of succinyl grafting. ^{1}H NMR (D$_2$O, 400 MHz, δ, ppm): 1.95 (H of acetyl groups), 2.46-2.52 (methylene protons of the succinyl), 2.97 (H2 of glucosamine, GlcN), 3.40-3.80 (H2′ of *N*-acetylglucosamine, GlcNAc, H3, H4, H5 and H6 of GlcNAc and GlcN), 4.40 (H1 of GlcNAc and GlcN).

N-succinylchitosan (N-SCS 2): 73% yields of yellow powder and 0.24 degree of succinyl grafting. ^{1}H NMR (D$_2$O, 400 MHz, δ, ppm): 1.98 (H of acetyl groups), 2.42-2.50 (methylene protons of the succinyl), 2.98 (H2 of glucosamine, GlcN), 3.40-3.83 (H2′ of *N*-acetylglucosamine, GlcNAc, H3, H4, H5 and H6 of GlcNAc and GlcN), 4.41 (H1 of GlcNAc and GlcN).

Encapsulation of *N*-eicosane with *N*-succinylchitosan by solvent displacement method.

Encapsulation at 1: 2 of polymer to PCM ratio.

For each NSCS, (N-SCS 1) and (N-SCS 2) 400 mg were dispersed into 25 mL of deionized water. *N*-eicosane (800 mg) was dissolved into 20 mL mixture solvent of ethylacetate to ethanol (1:2 V/V). Then *N*-eicosane solution was added into NSCS solution and then 80 mL of deionized water was slowly dropped into the mixture while the mixture was continuously homogenized by homogenizer at 6000 rpm for 30 min. The

sample was characterized by scanning electron microscopic (SEM, JEM 6400, JEOL, Tokyo, Japan) and optical microscope.

Encapsulation of *N*-eicosane with *N*-succinylchitosan by a novel liquid to solid encapsulation process.

Encapsulation at 1: 2 of polymer to PCM ratio.

(NSCS 1) 400 mg was dispersed into 100 mL of deionized water. *N*-eicosane (800 mg) was added into NSCS 1 solution which was maintained at 60 ºC. The mixture was continuously homogenized by homogenizer at 6000 rpm and the temperature was maintained at 60 ºC. Then the emulsion was cooled down to 0 ºC while the mixture was still homogenized at the same speed for another 15 min.

2.2.2 Ethyl cellulose shell

Encapsulation of *N*-eicosane with Ethyl cellulose by solvent displacement method.

Encapsulation at 1: 2 of polymer to PCM ratio.

Two hundred milligrams of EC was dissolved in 75 mL of ethanol. *N*-eicosane (400 mg) was dissolved into 25 mL mixture solvent of ethylacetate to ethanol (1:2 V/V). Then *N*-eicosane solution was added into EC solution while the mixture was continuously homogenized by homogenizer at 6000 rpm for 30 min. Then the suspension was dialyzed against deionized water (5×1000 mL) to remove ethylacetate and ethanol.

Encapsulation of *N*-eicosane with Ethyl cellulose by liquid to solid encapsulation process.

Encapsulation at 1: 2 of polymer to PCM ratio.

Two hundred milligrams of EC was dissolved in 25 mL of ethanol Then, *N*-eicosane (400 mg) was added into EC solution which was maintained at 60 ºC. Then 80 mL of hot water (80 ºC) was slowly dropped into the mixture while the mixture was continuously homogenized by homogenizer at 6000 rpm and the temperature was maintained at 60 ºC. Then the emulsion was cooled down to 0 ºC while the mixture was

still homogenized at the same speed for another 15 min. The obtained encapsulated *N*-eicosane (encap- *N*-eicosane) suspension was subjected to ethanol removal under vacuum and the water suspension was either freeze-dried or centrifuged and dried under vacuum to remove water.

2.2.3 Blend of ethyl cellulose and methyl cellulose shell

Encapsulation of *N*-eicosane with Ethyl cellulose by solvent displacement method.

Encapsulation at 1: 2 of polymer to PCM ratio.

Two hundred sixty six milligrams of EC was dissolved in 65 mL of ethanol then 133 milligrams of the MC were dissolved in10 mL of distilled water and stirred until clear transparent solution was obtained. *N*-eicosane (800 mg) was dissolved into 25 mL mixture solvent of ethylacetate to ethanol (1:2 V/V). Then *N*-eicosane solution was added into EC/MC solution while the mixture was continuously homogenized by homogenizer at 6000 rpm for 30 min. Then the suspension was dialyzed against deionized water (5×1000 mL) to remove ethylacetate and ethanol.

Encapsulation of *N*-eicosane with Ethyl cellulose by liquid to solid encapsulation process.

The microencapsulation of *N*-eicosane was carried out at various polymers to PCM ratios. *Encapsulation at 1: 4 of polymer to PCM ratio.*

Two hundred sixty milligrams of EC were dissolved in 35 mL of ethanol then 133 milligrams of the MC were dissolved in10 mL of distilled water and stirred until clear transparent solution was obtained. Then, *N*-eicosane (1.6 g) was added into polymeric solution which was maintained at 60 ℃. Then 80 mL of hot water (80 ℃) were slowly dropped into the mixture while the mixture was continuously homogenized by homogenizer at 6000 rpm and the temperature was maintained at 60 ℃. Then the emulsion was cooled down to 0 ℃ while the mixture was still homogenized at the same speed for another 15 min. The obtained encapsulated *N*-eicosane (encap- *N*-eicosane) suspension was subjected to ethanol removal under vacuum and the water suspension was freeze dried. The dry samples was characterized by scanning electron microscopic (SEM,

JEM 6400, JEOL, Tokyo, Japan), transmission electron microscopic (TEM, HITACHI, H-7650, 100 kV,Canada), differential scanning calorimetry (at the heating and cooling rate of 10 $^{\circ}$C/ min under nitrogen atmosphere (20 mL/min), METTLER, DSC 822, USA) and X-ray powder diffraction (XRD, a Rigaku DMAX 2200/Ultima+ diffractometer, Rigaku International Corporation, Tokyo, Japan), dynamic light scattering (DLS) analysis.

Encapsulation at 1: 10 of polymer to PCM ratio.

Two hundred sixty six milligrams of EC were dissolved in 35 mL of ethanol then 133 milligrams of the MC were dissolved in10 mL of distilled water and stirred until clear transparent solution was obtained. Then, *N*-eicosane (4.0 g) was added into polymeric solution and next step was done similar to encapsulated 1: 4 of polymer to PCM ratio.

Encapsulation at 1: 20 of polymer to PCM ratio.

Two hundred sixty six milligrams of EC were dissolved in 35 mL of ethanol then 133 milligrams of the MC were dissolved in10 mL of distilled water and stirred until clear transparent solution was obtained. Then, *N*-eicosane (8 g) was added into polymeric solution and next step was done similar to encapsulated 1: 4 of polymer to PCM ratio.

2.2.4 Encapsulation of Paraffin wax

Blend of ethyl cellulose and methyl cellulose shell

The microencapsulation of Paraffin wax was carried out by a liquid to solid encapsulation process at two polymers (EC and MC) to Paraffin wax weight ratios, 1:10. Two hundred sixty six milligrams of EC were dissolved in 25 mL of ethanol then 133 milligrams of the MC were dissolved in10 mL of distilled water and stirred until clear transparent solution was obtained. Then Paraffin wax (3.99 g) was added into polymeric solution which was maintained at 60 ºC for *N*-eicosane,. Then 80 mL of hot water (80 ºC) were slowly dropped into the mixture while the mixture was continuously homogenized by homogenizer at 6000 rpm and the temperature was maintained at 75 ºC. Then the emulsion was cooled down to 0 ºC while the mixture was still homogenized at the same

speed for another 15 min. The obtained encapsulated Paraffin wax suspension was subjected to ethanol removal under vacuum and the water suspension was freeze dried. The dry sample was characterized by SEM, TEM, DSC, XRD and DLS analysis.

2.3 Finding the optimum ratio between Ethylcellulose and methylcellulose

For finding the optimum ratio between ethylcellulose and methylcellulose (as shell material), the weight ratio of ethylcellulose and methylcellulose of 1:1, 2:1, and 5:1 were investigated.

2.4 Morphology of PCM-microcapsule

The morphology of encap-C_{20} was determined with scanning electron microscope (SEM) and transmission electron microscope (TEM). Particle size distribution and the ζ potential were determined by Zetasizer nano series (Malvern Instruments).

TEM photographs were acquired on a transmission electron microscope (HITACHI, H-7650, 100 kV, Japan). A drop of encap-C_{20} suspension was placed on a carbon film coated on a copper grid and dried. Observation was performed at 100 kV.

SEM photographs were obtained using a scanning electron microscope (JEM-6400, JEOL, Tokyo, Japan). A drop of the encap-C_{20} suspension was placed on a glass slide and dried. The sample was coated with a gold layer under vacuum at 15 kV for 90 s.

An average particle size (z-average size) was measured by Zetasizer (Nano Series Model) (Malvern Instruments, Worcestershire, UK) equipped with a He-Ne laser beam at 632.8 nm (scattering angle of 173º) at 25 ± 2ºC. Each measurement was repeated three times and an average value was reported.

2.5 Determination of thermal properties of the microcapsules

The phase change properties of the dried PCM-microcapsules such as melting and freezing points and latent heats, were obtained by differential scanning calorimeter (METTLER, DSC 822). Two milligrams of the dried encap-PCM were precisely weight into aluminum cups and sealed. A small hole was done at the top of the cup in order to allow the release of water. An empty cup was used as reference. The experiment

consisted of two runs. The first one heat up from -50 to 150°C and the second one cool down from 150 to -50°C. The experiments were run at the heating and cooling rate of 10 °C/ min, under nitrogen atmosphere (20 mL/min).

2.6 Recycling of the microcapsules

The dried PCM-microcapsules were subjected to repeated cycle of melting and solidification (heat to 50 ºC for 5 min and then cooled to 25 ºC for 5 min). This process was repeated for 200 times and PCM-microcapsules were characterized by SEM and DSC analysis. Water dispersion ability of the repeated heat-cool cycle PCM-microcapsules was tested by dispersing PCM-microcapsules in distilled water.

2.7 Preparation of Thermo-regulated NR
2.7.1 Preparation of Thermo-regulated NR by mixing the dried encap-PCM

Thermo-regulated NR was prepared at two ratios, 1:1 and 1:2 NR to encap C20 and NR to encap Paraffin wax by adding the dried encap-PCM into NR latex. The 60% DRC NRL 60 g of the dry rubber matter in 100 mL latex was mixed with dried encap-C20 by stirring for 20 min.

2.7.2 Preparation of Thermo-regulated natural rubber by mixing the encap-PCM suspension

Thermo-regulated NR was prepared at two ratios, 1:1 and 1:2 of NR to encap – C20 and NR to encap – Paraffin wax by mixing the encap-PCM suspension with NR latex. The amount of materials used in the preparation of thermo-regulated NR was shown in Table 3. The 60% DRC NR latex was mixed with water slurry of encap-C20 by stirring for 20 min. Then, the solution was poured into a 14 × 14 × 0.2 cm mold and air-dry at 25 ºC. The obtained rubber sheet was then subjected to determine the mechanical properties by Universal Tasting Machine (LR 10K PLUS, England). The thermoregulation test of the PCM-rubber piece was carried out using a circle rubber piece (diameter of 5.2 cm and thickness of 0.315 cm). The control rubber was the rubber piece with no PCM microspheres added.

Table 2.1 Recipe for the preparation of thermo-regulated natural rubber

material	Content (g)	
	Ratio of NR to encap – C20, 1:1	Ratio of NR to encap – C20, 1:2
60 DRC NR latex	12	12
Encap – C20 (or Encap – Paraffin wax)	7.2	15.4
water	2	4

2.8 Dispersion of PCM capsules in the rubber piece

The dispersion of PCM microspheres in PCM-rubber piece was analyzed by SEM. The fractured surface of the PCM-rubber piece was fractured under liquid nitrogen. The fractured samples were sputter-coated with gold. The images recorded by SEM (JEM-6400, JEOL, Tokyo, Japan). The SEM images were used to estimate the degree of PCM particle dispersion.

2.9 Thermo-regulation test of the PCM-rubber piece

The PCM-rubber piece and the control rubber were tested using a circle rubber piece (diameter of 5.2 cm and thickness of 0.315 cm). The control rubber piece and the PCM-rubber piece with the temperature of 29 °C were put onto a temperature controlled surface which was maintained at 50 - 52 ºC. Both rubber samples were then characterized by thermal camera (ISI, Infrared Solutions SnapShot®, USA) at various times. For the releasing heat of PCM-rubber piece and control rubber, the rubber pieces with temperature of 47 °C was left at room temperature (29 °C). The releasing heat of rubber samples were characterized by thermal camera at various times.

2.10 Thermal stability test of the PCM microspheres in PCM-rubber piece

The thermal stability test of PCM microspheres in PCM-rubber piece was analyzed by keeping the PCM-rubber piece (diameter of 5.2 cm and thickness of 0.315 cm) in oven at 80 and 100 °C for 20 min in order to check the stability of PCM microspheres in PCM-rubber piece after curing.

2.11 Tensile Measurement

Tensile test was analyzed by Universal Tasting Machine LR 10K PLUS, England. In accordance with ASTM-D412 at room temperature and a crosshead seed of 500 mm/min. Tensile testing is accomplished by molding a flat sheet of rubber about 2 mm thick, from which dumbbell shaped pieces were cut (show in Figure 2.1)
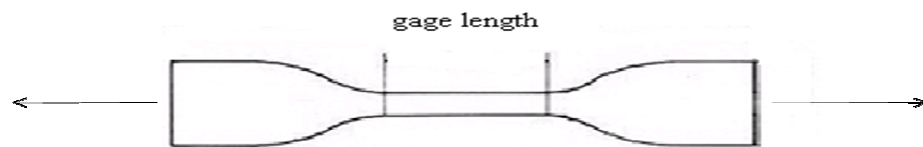
Figure 2.1 Dumbbell shaped test pieces for tensile testing.

CHAPTER III

RESULT AND DISCUSSION

We have prepared the PCM microcapsules of N-eicosane and paraffin using various polymeric shell materials. The shell materials included N-succinylchitosan, ethyl cellulose, and methyl cellulose. These biopolymers are biocompatible, harmless to human and non toxic to the environment.
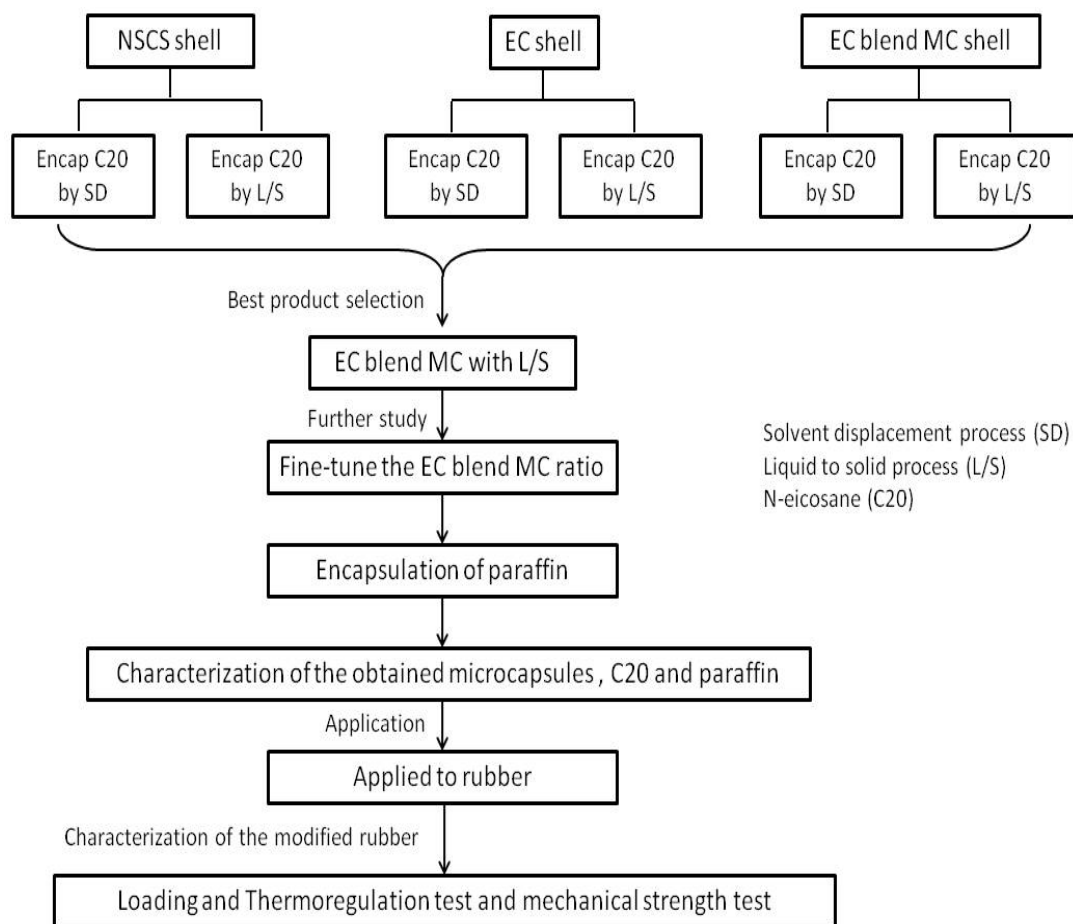
Scheme 3.1 Over view of the research.

3.1 *N*-succinylchitosan as shell material

Preparation and characterization of *N*-succinylchitosan
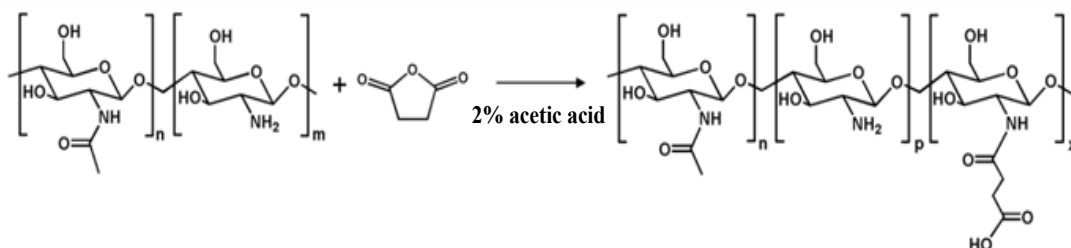
Scheme 3.2 Preparation of *N*-succinylchitosan

The *N*-succinylchitosan was prepared via a succinylation reaction between amino group and succinic anhydride to form *N*-succinylchitosan (N-SCS). Two N-SCS with different degrees of succinylation, namely N-SCS1 and N-SCS2, were prepared. The reaction is presented in Scheme 3.1.

The *N*-succinylchitosan (N-SCS1) structure was confirmed by ^{1}H NMR. The ^{1}H NMR spectrum of N-SCS1 in D_2O shows signals at 2.42-2.50 ppm which can be assigned to dimethylene protons of the grafted succinyl group. Using the integral ratio between 4H from ethyl group of succinyl and 1H from C2 of glucosamine unit (at 2.98 ppm), the degree of grafting could be estimated as 0.43.
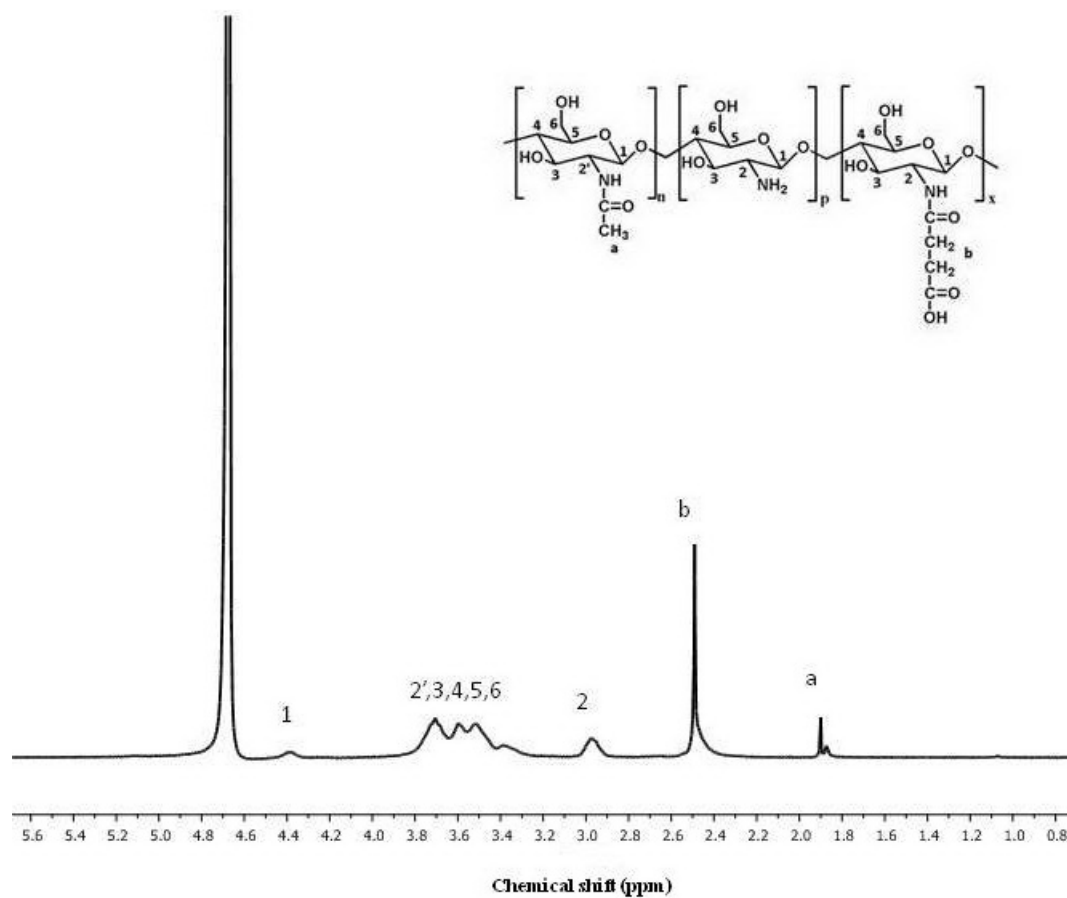
Figure 3.1 ^{1}H NMR spectrum of N-SCS1.

Similarly, the drgree of succinylation in N-SCS2 could be estimated as 0.24. The *N*-SCS1 and N-SCS2 were then used as shell material for the encapsulation of *N*-eicosane. Two encapsulation processes were tried, the solvent displacement and the novel liquid to solid encapsulation process.

Figure 3.2 ^{1}H NMR spectrum of N-SCS2.

Encapsulation of N-eicosane with N-succinylchitosan by solvent displacement method.

The formation of N-eicosane into N-SCS shell was also prepared through solvent displacement method. The hydrophobic parts of N-SCS chain interacted with *N*-eicosane while solution of *N*-eicosane and N-SCS were slowly added water into the *N*-eicosane / N-SCS suspension under homogenizing condition, the hydrophilic parts of the polymer form the hydrogen bonding with water molecules.

The encapsulation of *N*-eicosane with NSCS1 and NSCS2 by solvent displacement method gave colloidal suspension but the colloidal suspension showed some waxy residue on the surface, probably the remaining unencapsulated *N*-eicosane. The suspension of the sample was characterized by SEM and optical microscope analysis. The optical microscope image showed the spherical particles in microscale size (Figure 3.3 and 3.4). The *N*-eicosane particles could not withstand the electron impact

during SEM analysis, they burst and melted during that process, therefore their SEM images are not clear (Figure 3.3). The optical microscope images, however showed a better morphology. The optical microscope images showed the spherical shape of the N-eicosane particle.
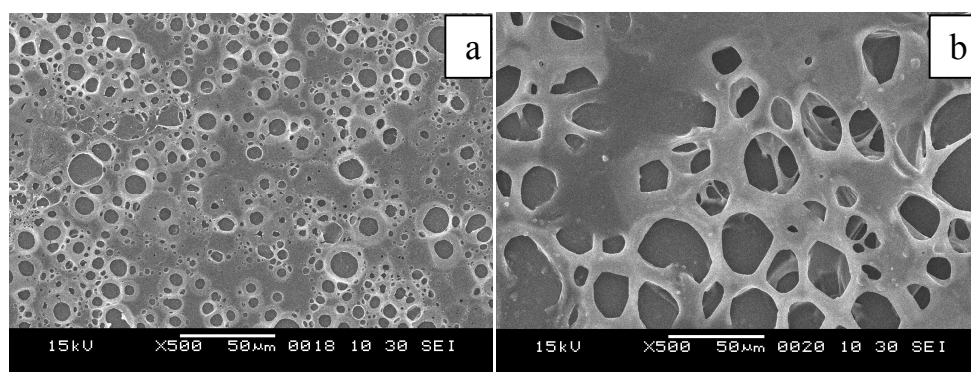
Figure 3.3 SEM images of N-SCS1 and N-SCS2 microparticles, (a) N-SCS1 microparticles (b) N-SCS2 microparticles.
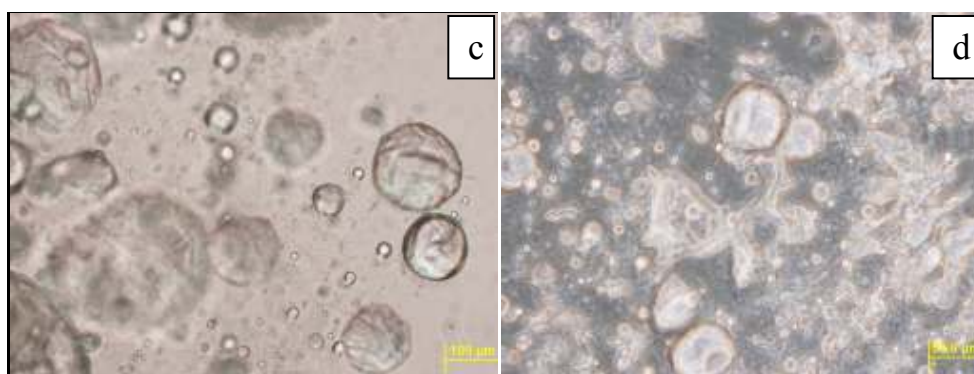
Figure 3.4 optical microscope images of N-SCS1 and N-SCS2 microparticles, (a) N-SCS1 microparticles and (b) N-SCS2 microparticles.

Encapsulation of N-eicosane with N-succinylchitosan by a novel liquid to solid encapsulation process.

The formation of *N*-eicosane into N-SCS shell was prepared through liquid to solid encapsulation process. When the *N*-eicosane was added into warm water solution of N-SCS under homogenizing condition, solidifying formed microspheres by lower the temperature of the system to 4 ˚C (lower than the melting temperature of the *N*-eicosane).The formation of *N*-eicosane microdroplets in warm water with simultaneous covering of N-SCS chains around the formed *N*-eicosane droplets, the N-SCS chains had time to arrange themselves in such a way that the hydrophobic side of the N-SCS chains interacts with the hydrophobic *N*-eicosane inside the microdroplets while the hydrophilic moieties of the N-SCS chains (hydroxyl moieties) interact with water medium at the outer surface of the microspheres. Such an arrangement makes the obtained microspheres dispersible in water medium without the need of any additional surfactant molecules. The novel liquid to solid encapsulation process was study in order to compare with solvent displacement method.

The *N*-eicosane encapsulated with both NSCS1 and N-SCS2 in aqueous system showed colloidal suspension but the colloidal suspension showed some waxy appearance in the surface. The result is similar to the encapsulation of *N*-eicosane with *N*-succinylchitosan by solvent displacement method. The SEM and optical microscope image showed the spherical particles in microscale size (Figure 3.5). The *N*-eicosane particles could not withstand the electron impact during SEManalysis, they burst and melt during that process.
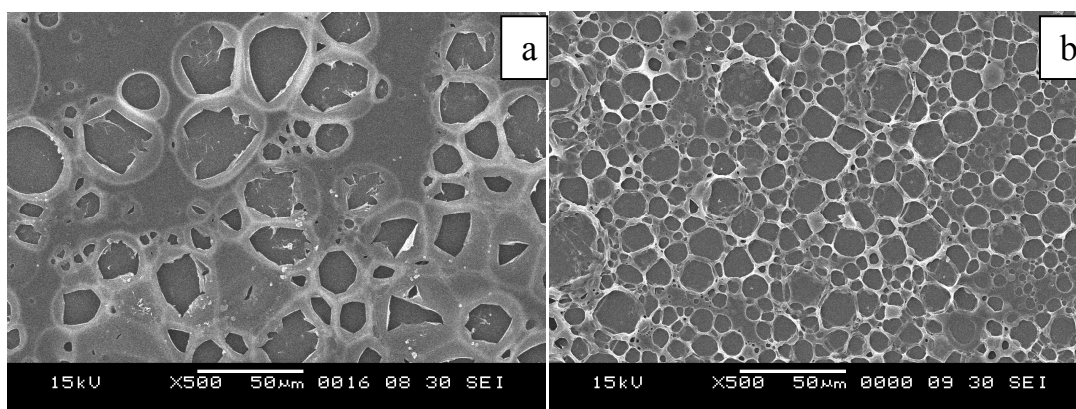
Figure 3.5 SEM images of N-SCS1 and N-SCS2 microparticles, (a) N-SCS1 microparticles (b) N-SCS2 microparticles.
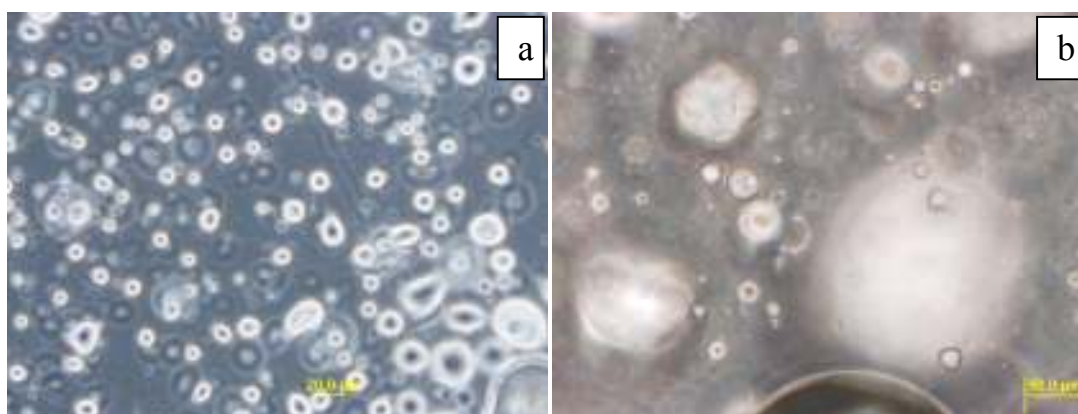
Figure 3.6 Optical microscope images of N-SCS1 and N-SCS2 microparticles, (a) N-SCS1 microparticles and (b) N-SCS2 microparticles

In conclusion, the *N*-succinylchitosan(N-SCS1 and N-SCS2) were not suitable for *N*-eicosane encapsulation because the *N*-succinylchitosan(N-SCS1 and N-SCS2) shell could not withstand the electron impact during SEM analysis which indicated the *N*-succinylchitosan(N-SCS1 and N-SCS2 were not strong shell for the *N*-eicosane encapsulation.

3.2 Ethyl cellulose as shell material

Ethyl cellulose was used as shell material for the encapsulation of *N*-eicosane. Two encapsulation processes were tried, the solvent displacement and the novel liquid to solid encapsulation processes.
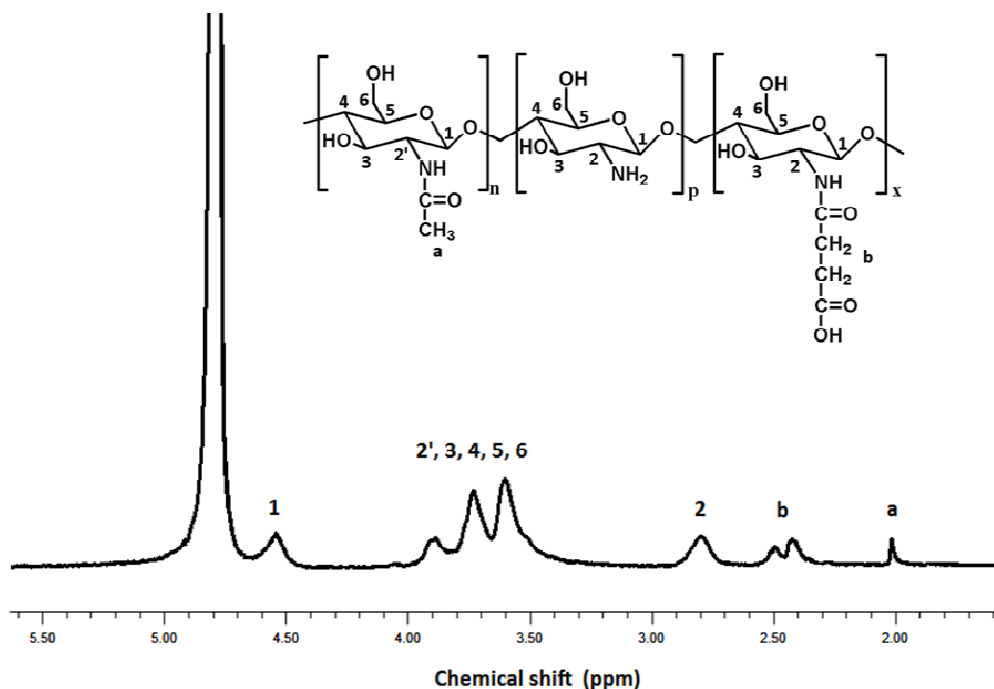
Encapsulation of N-eicosane with ethyl cellulose by solvent displacement method.

The formation of *N*-eicosane into EC shell was prepared through solvent displacement method. The ethanolic solution of *N*-eicosane and polymers were slowly displaced with water across the dialysis membrane. When the polarity of the medium increases, the polymer chains had time to arrange themselves in such a way that the hydrophobic side of the EC polymer (ethyl moieties) interacts with the hydrophobic *N*-eicosane inside the microdroplets while the hydrophilic moieties of the EC chains (hydroxyl moieties) interact with water medium at the outer surface of the microspheres. Such an arrangement makes the obtained microspheres dispersible in water medium.

The Encapsulation of *N*-eicosane with ethyl cellulose by solvent displacement method although showed colloidal suspension but the colloidal suspension contained some waxy appearance on the surface, indicating probably the remaining unencapsulated *N*-eicosane from the encapsulation. In addition some EC chain cannot interact with *N*-eicosane, thus some materials percipitated at the bottom. Therefore, this method was not suitable for *N*-eicosane encapsulation by EC.

Encapsulation of N-eicosane with ethyl cellulose by liquid to solid encapsulation process.

The formations of N-eicosane into EC by liquid to solid encapsulation process gave similar result to the formations of N-eicosane into ethyl cellulose by solvent displacement method. The encapsulation of *N*-eicosane with ethyl cellulose by liquid to solid encapsulation process showed colloidal suspension with some EC precipitates at the bottom.. The formation of *N*-eicosane into EC shell by liquid to solid encapsulation process, therefore, were not suitable.

3.3 Ethyl cellulose/methyl cellulose-blend as shell material

Ethyl cellulose/methyl cellulose-blend was used as shell material for the encapsulation of *N*-eicosane. Two encapsulation processes were tried, the solvent displacement and the novel liquid to solid encapsulation process.

Encapsulation of N-eicosane with Ethyl cellulose blend methyl cellulose by solvent displacement method.

The formations of N-eicosane into EC/MC blend shell by solvent displacement method gave colloidal suspension with big gelatinous masses together with some waxy materials on the surface. The waxy matter was the remaining unencapsulated *N*-eicosane from encapsulation. This method, therefore, was not suitable for *N*-eicosane encapsulation.

Encapsulation of N-eicosane with Ethyl cellulose/methyl cellulose-blend by liquid to solid encapsulation process.

N-eicosane encapsulated into EC/MC blend shell (encap- *N*-eicosane) was successfully prepared through our novel liquid to solid encapsulation process. The process involved slowly adding warm water into warm ethanolic solution of PCM and polymers under homogenizing condition, then solidifying the formed microspheres by lower the temperature of the system to 4 ˚C (lower than the melting temperature of the *N*-eicosane).The mechanism involves the formation of *N*-eicosane microdroplets in warm water with simultaneous covering of EC polymeric chains around the formed *N*-eicosane droplets. When the polarity of the medium increases slowly during the slow addition of water into the *N*-eicosane /polymer suspension, the polymer chains had time to arrange themselves in such a way that the hydrophobic side of the EC polymer (ethyl moieties) interacts with the hydrophobic *N*-eicosane inside the microdroplets while the hydrophilic moieties of the EC chains (hydroxyl moieties) interact with water medium at the outer surface of the microspheres. Such an arrangement makes the obtained microspheres dispersible in water medium without the need of any additional surfactant molecules. During the self-assembling of the EC around the *N*-eicosane droplets, the MC chains are likely to be trapped and entangled into the polymeric shell of the microspheres. The

presence of the MC chains at the polymeric wall of the microspheres helps the spheres to be more stably dispersible in water.

The encapsulation of *N*-eicosane with ethyl cellulose/ methyl cellulose blend by liquid to solid encapsulation process showed homogeneous colloidal suspension with no precipitation, therefore, the EC/MC blend shell was suitable for *N*-eicosane encapsulation using liquid to solid encapsulation process. As a result, the PCM microcapsules prepared by liquid to solid encapsulation process using EC/MC blend shell were further investigated in this research.

3.4 Finding the optimum ratio between Ethylcellulose and methylcellulose

The optimal ratio between ethylcellulose and methylcellulose for the PCM microparticle formation was investigated. Three ratios, 1:1, 2:1 and 5:1 were compared by evaluating the precipitation of EC/MC blend in the suspension. The best ratio between ethylcellulose and methylcellulose was 2:1, since the obtained suspension showed no precipitates. Therefore the PCM microcapsules prepared at the weight ratios of ethylcellulose to methylcellulose of 2:1 was further investigated in this research.

Encapsulation of Paraffin wax

Paraffin wax is the most used commercial organic heat storage PCM. It consists mainly of straight chain hydrocarbons that have melting temperatures ranging from 23 to 67 °C. Paraffins are easily available from many manufacturers and are usually less inexpensive than pure *N*-eicosane. Paraffin was, therefore, further investigated in this research.

The encapsulation of paraffin into EC/MC blend shell with paraffin: polymer weight ratios of 10:1 by liquid to solid encapsulation process gave colloidal suspension with some paraffin remained unencapsulated on top of the suspension (waxy matter).

3.5 The morphology of microcapsules

The colloidal suspension of the obtained *N*-eicosane and paraffin encapsulated into ethyl cellulose/methyl cellulose-blend by liquid to solid encapsulation process was subjected to SEM and DLS analyses. The preparation of three *N*-eicosanes:polymers, weight ratios 4:1, 10:1and 20:1, which had 20%, 9% and 4.76% weight contents of polymer material (EC and MC) respectively corresponded to the final dry products with *N*-eicosane loading of 80%, 91% and 95.24% by weight, respectively. SEM and TEM analyses of the encapasulated *N*-eicosane showed core-shell microspherical architecture (Figure 3.7) with the diameters of 4.73±0.62 and 5.92±1.15 μm for the particles with 20 and 9 % polymer, respectively. Dynamic light scattering analysis gave agreeable particle sizes of 7.69 ± 5.95 and 6.78 ± 2.90 μm for the 20 and 9% polymer particles, respectively (Table 3.1). Particles size obtained from DLS was bigger than particles size from SEM. The result concluded that the encap- *N*-eicosane spheres could swell in water medium. Whereas SEM characterization, used dried sample gave smaller particles size. The *N*-eicosane:polymer weight ratio 20:1was not characterized because the dry products dispersed poorly in water medium.

The particles with paraffin wax:polymer, weight ratio of 10:1 were prepared. SEM and TEM analysis of the products showed the microspherical architecture core-shell with the diameters of 3.71±0.79 μm (Figure 3.8). Dynamic light scattering analysis gave agreeable particle sizes of 6.17 ± 2.37 μm. The zeta potential of obtained suspension in water was -10.04 mV

Hydrodynamic diameters and Zeta potential of the encapsulte *N*-eicosane and encapsulated paraffin obtained by DLS are shown in Table 3.1. Theoretically, the high negative or positive zeta potential of the microparticles will make them repel each other and thus minimize their aggregations. Normally the zeta potentials of stable suspension should be more positive than +30 mV or more negative than -30 mV [38]. The obtained zeta potentials of the obtained suspension was below -30 mV, indicating unstable suspension of the two particles in water medium. The encapsulated *N*-eicosane and encapsulated paraffin suspension can aggregate when the suspension was left for 1 hr, however, upon stirring they all dispersed back into water nicely.
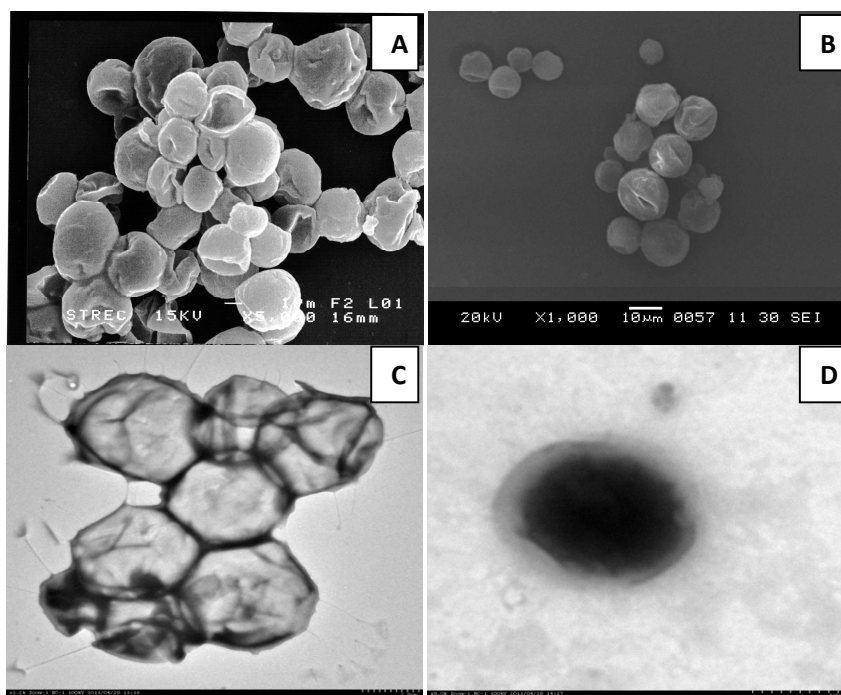
Figure 3.7. SEM and TEM images of encapsulated *N*-eicosane, (A) SEM image of *N*-eicosane:polymer weight ratios 4:1, (B) SEM image of *N*-eicosane:polymer weight ratios 10:1, (C) TEM image of *N*-eicosane:polymer weight ratios 4:1, (D) TEM image of *N*-eicosane:polymer weight ratios 10:1.
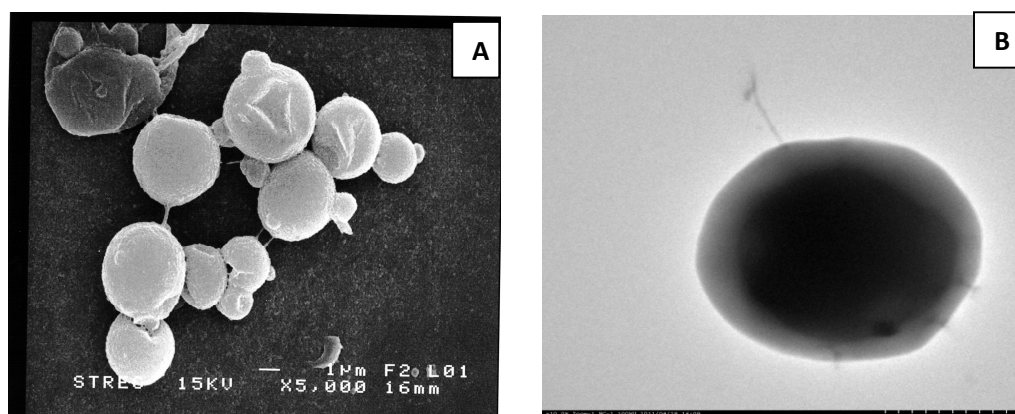
Figure 3.8. SEM and TEM images encapsulated paraffin, (A) SEM image of Paraffin wax:polymer weight ratios 10:1, (B) TEM image of Paraffin wax:polymer weight ratios 10:1.

Table 3.1 Hydrodynamic diameters and Zeta potential the microcapsules

Spheres	Hydrodynamic diameter	Zeta potential
	(µm.)	(mV)
N-eicosane:polymer weight ratios 4:1	7.69 ± 5.95	-10.60± 1.22
N-eicosane:polymer weight ratios 10:1	6.78 ± 2.90	-10.73± 0.93
Paraffin:polymer weight ratios 10:1	6.17 ± 2.37	-10.04±0.58

3.6 Determination of thermal properties of the microcapsules

The thermal properties of the PCM-microcapsules were evaluated by differential scanning calorimetry (DSC). The DSC curves of the pure N-eicosane and EC/MC blend are shown in   Figure 3.8.
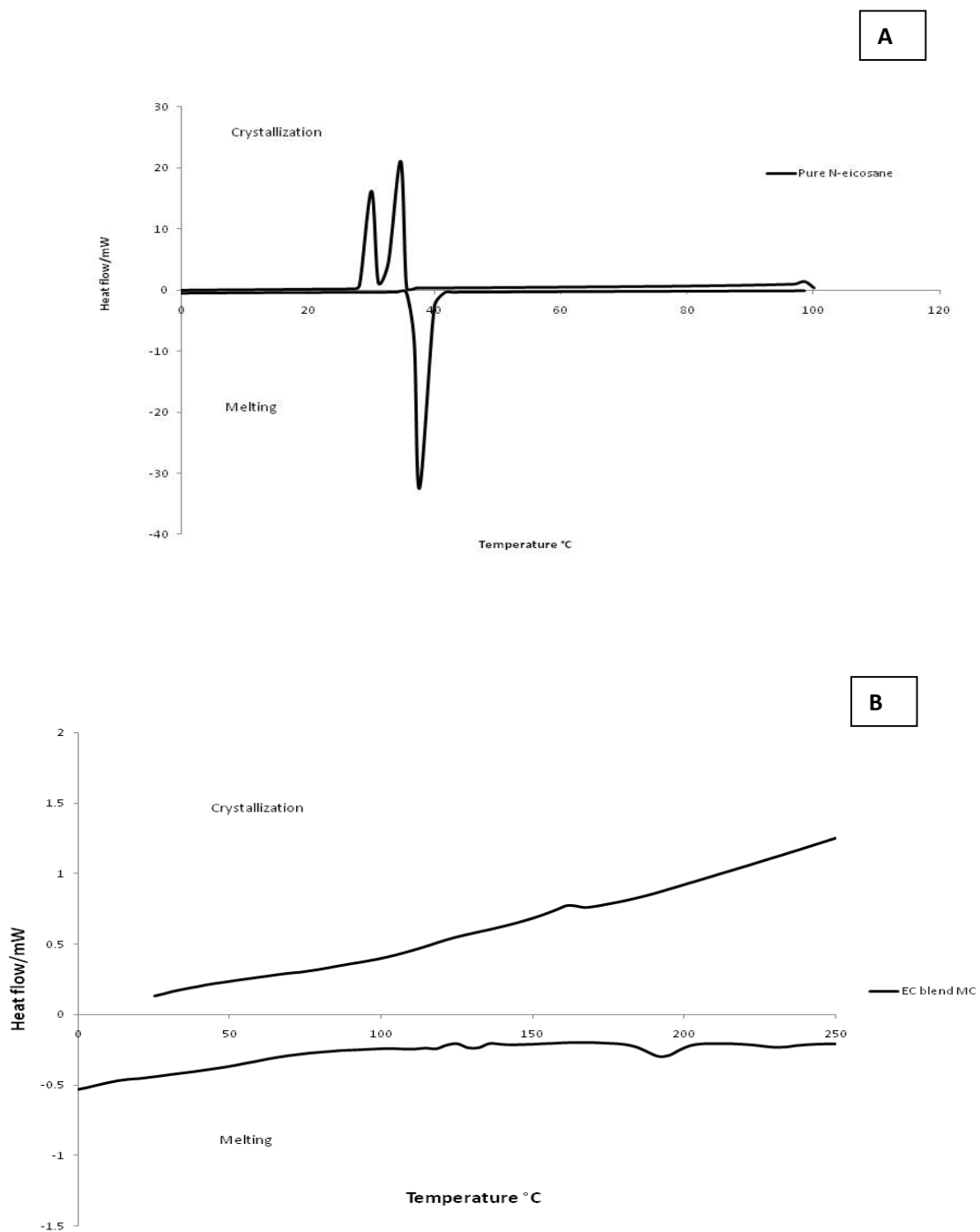
Figure 3.9 The DSC curves of the pure *N*-eicosane (A) and EC/MC blend (B)

The DSC curves of the pure *N*-eicosane and EC/MC blend at 30-45 °C showed only enthalpy values of pure *N*-eicosane, indicating that the enthalpy values at 30-45 °C (figure 3.9).
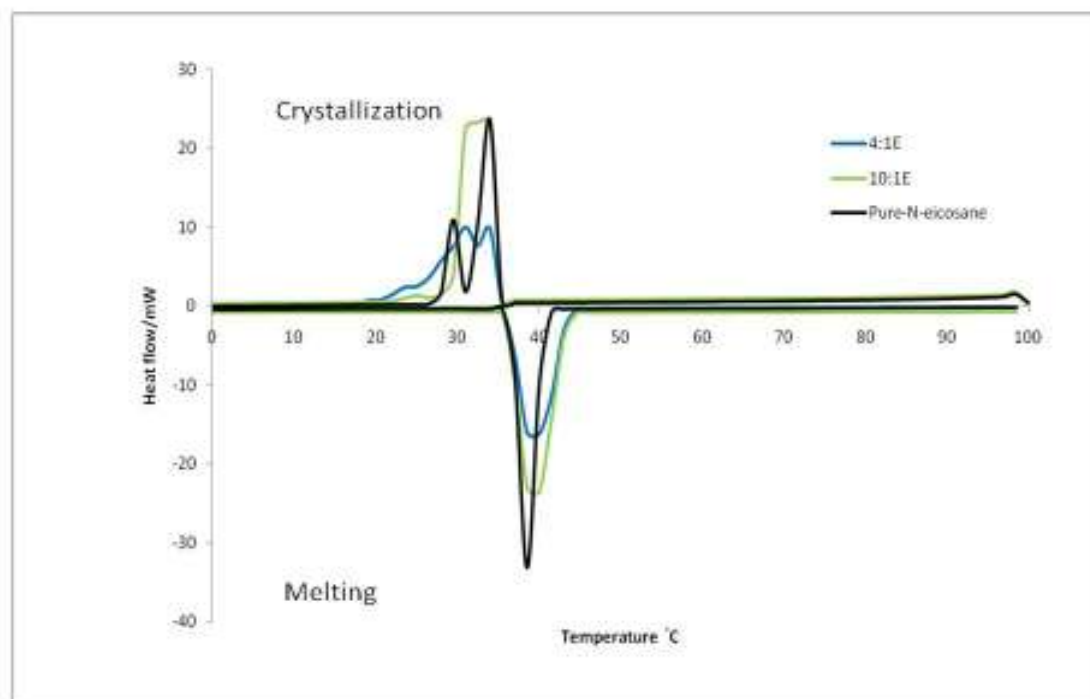
Figure 3.10 DSC curves of *N*-eicosane, *N*-eicosane:polymer (4:1)W/W, *N*-eicosane:polymer (10:1)W/W.

The DSC curves of the encapsulated *N*-eicosane are shown in Figure 3.10. The melting temperature, crystallizing temperature, melting enthalpy and crystalline enthalpy were tabulated in Table 3.2. The thermogram curves of the *N*-eicosane showed an exothermic crystallization. The first transition was the formation of rotator phase at 34.2 °C and the second transition was the formation of stable phase (triclinic crystal) [39] at 30.6 °C (Figure 3.9). The enthalpy of the transition into the rotator phase during the cooling down was -50.47 ± 4.02 J/g, while the second transition was -135.61 ± 6.10 J/g. The endothermic melting showed only single transition at 38 °C with an enthalpy value of 202.37 ± 5.95 J/g which was closed to the total enthalpy value of the two step crystallization (-186.07 ± 2.08 J/g). The freezing range (20-35 °C) and the melting range

(35-45 °C) of the two encapsulated *N*-eicosane microspheres were wider than that of the pure *N*-eicosane (Figure 3.9). This indicated interaction between the polymer chains and the *N*-eicosane molecules. The exothermic crystallization of the encap-C20 led to a multiple but overlapped transitions at 20- 35 ˚C with the total absolute enthalpy values of -204.54 ± 8.46 J/g and -239.82 ± 3.76 J/g, which corresponded to the 9.93 and 28.89 % increased, comparing to the value of the pure *N*-eicosane of -186.07 J/g. The encapsulated *N*-eicosane prepared at the *N*-eicosane:polymer weight ratios of 4:1and 10:1, respectively. The increase in the absolute enthalpy value during the phase transition of the encapsulated *N*-eicosane was also true for the heating process. When the temperature of the system increased, the bulk *N*-eicosane showed single transition with an enthalpy value of 202.37 ± 7.29 J/g while the encapsulated *N*-eicosane prepared at the *N*-eicosane:polymer weight ratios of 4:1 and 10:1showed a single transition with enthalpy values of 208.22 ± 9.36 J/g and 251.42 ± 6.19 J/g, which corresponded to the 2.89 and 24.24 % increased in the energy storage capacity, respectively.

Table 3.2 DSC results of PCMs.

Material	Loading (% wt)	Transition interval (˚C)	Peak T_c (˚C)	Peak T_m (˚C)	Enthalpy (J /g)	
					endothermic	exothermic
Unencapsulated C20	100	36.50-40.5	30.6, 34.2	37.87	202.37 ± 5.95	-186.07 ± 2.08
Encap-C20 at C20:polymer wt ratio of 4:1	80	36.35-43.3	31.0, 34.0	39.00	208.22 ± 9.36	-204.54 ± 8.46
Encap-C20 at C20:polymer wt ratio of 10:1	91	36.24-43.6	32.5, 34.0	38.79	251.42 ± 6.19	-239.82 ± 3.76
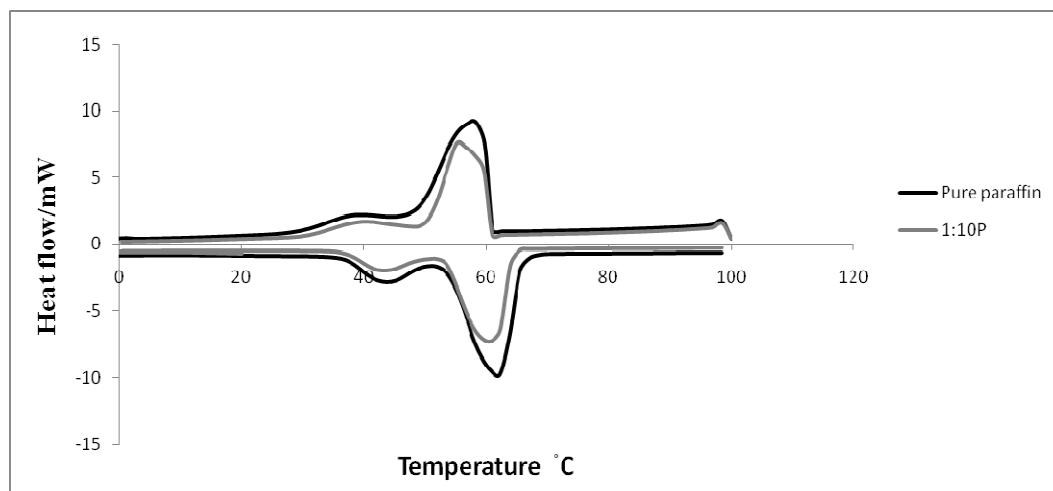
Figure 3.11 DSC curves of Paraffin, Polymer: Paraffin (1:10) W/W

The thermogram curves of the paraffin showed an exothermic crystallization. At first transition was the rotator phase at 37.88 °C and the second transition was the stable phase of triclinic crystal at 58.41 °C (Figure 3.11). The enthalpy of the transition into the rotator phase during the cooling down was -8.66 ± 1.18 J/g, while the second transition was -135.51 ± 2.06 J/g. The endothermic melting was at 45.43 °C and 62.69 °C with an enthalpy value of 158.36 ± 0.68 J/g which was closed to the total enthalpy value of the two step crystallization (-144.16 ± 3.23 J/g). The endothermic crystallization of encapsulated paraffin showed an exothermic crystallization. At first transition was the rotator phase at 39.71 °C and the second transition was the stable phase of triclinic crystal at 60.95 ° C (Figure 3.10). The enthalpy of the transition into the rotator phase during the cooling down was -16.54 ± 0.63 J/g, while the second transition was -114.83 ± 1.77 J/g. The endothermic melting showed at 42.94°C and 60.77 °C with an enthalpy value of 138.12 ± 2.31 J/g which was closed to the total enthalpy value of the two step crystallization (-131.37 ± 2.40 J/g) which corresponded to the 8.54% decreased in the energy storage capacity, respectively.

3.7 The crystallinity of microcapsules

The crystallographic structure of pure *N*-eicosane, EC/MC blend shell and the encapsulated *N*-eicosane were determined using X-ray powder diffraction (XRD) analysis (Figure 3.12). The XRD pattern of EC blend MC exhibited broad peaks at 2θ of

7.8^o and 20°. Pure *N*-eicosane exhibited peaks at 2θ of 6.26°, 19.22°, 19.7°, 20.5°, 22°, 23.04°, 24.42°, and 34.4°. Peaks at 2θ of 6.74°, 10.36°, 13.6°, 17.04°, 20.5°, 34.42°, and 39.62° were obvious in the XRD pattern of encapsulated *N*-eicosane.

The XRD patterns of encapsulated *N*-eicosane indicated more crystallinity of the material comparing to pure *N*-eicosane. It was speculated that interaction of C20 and polymeric wall affected to crystallinity of *N*-eicosane inside the spheres. The difference in crystallinity of encapsulated *N*-eicosane and pure *N*-eicosane was the result in the differences in the observed melting enthalpy. It was speculated that the interaction of *N*-eicosane and polymeric wall material interferes the solidification of *N*-eicosane inside the spheres in such a way that make transition to be multistep and more exothermic with solid product of different XRD pattern than that of the pure *N*-eicosane. The melting of crystalline *N*-eicosane inside the spheres was also more endothermic comparing to the melting of the pure *N*-eicosane.
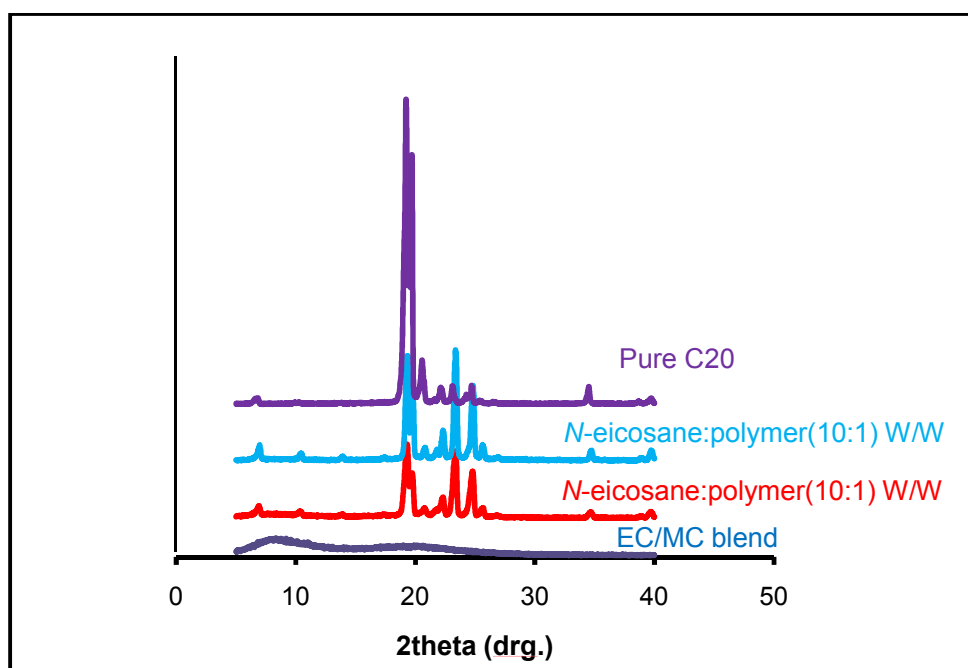
Figure 3.12 X-ray diffraction patterns of the pure *N*-eicosane, the EC and MC blend and the two encapsulated *N*-eicosane samples.
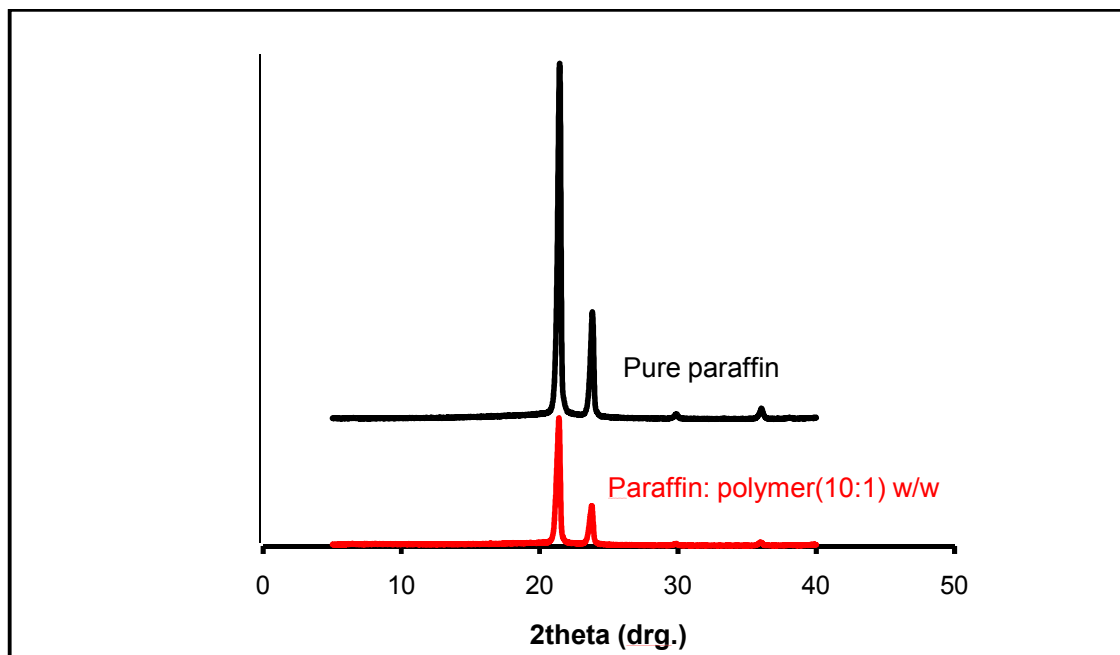
Figure 3.13 X-ray diffraction patterns of the pure paraffin, the encapsulated paraffin samples.

The Figure 3.13 showed the X-ray diffraction patterns of the pure paraffin and the encap paraffin. The XRD pattern of pure paraffin exhibits peaks at 2θ of 21.42^{o}, 23.76^{o}, 29.42^{o} and 35.58^{o}. The encapsulated paraffin exhibits peaks at 2θ of 21.38^{o}, 23.72^{o}, 28.92^{o} and 35.74^{o}. The situation of paraffin is different from that of C20. The free and loaded paraffin showed similar XRD pattern and encapsulation did not increase the enthalpy of phase transition of the material. Instead, enthalpy decreased upon encapsulation and this is likely to be the contribution from the polymer mass.

3.8 Recycling of the microcapsules

The encapsulated N-eicosane into EC/MC blend by liquid to solid encapsulation process gave particles with good thermal stability, the average latent heats of melting and freezing of the N-eicosane microcapsule prepared at the PCM to polymer weight ratio of 1:4 was subjected to stability evaluation. After 200 repeated thermal cyclings, its enthalpy value of melting and crystallization were 212.80 J/g and 207.13 J/g, respectively. The values were similar to those obtained from the untreated N-eicosane microcapsules. More importantly, the material still showed good water dispersibility

which indicated no leakage of the N-eicosane from the microspheres. In contrast, the heat treated microcapsule of encapsulated *N*-eicosane and encapsulated paraffin prepared at the PCM to polymer weight ratio of 10:1 showed the leakage of the liquid N-eicosane (poor dispersion in water). It was thus concluded that the polymeric wall must be thick enough to prevent the leaking of the encapsulated *N*-eicosane.
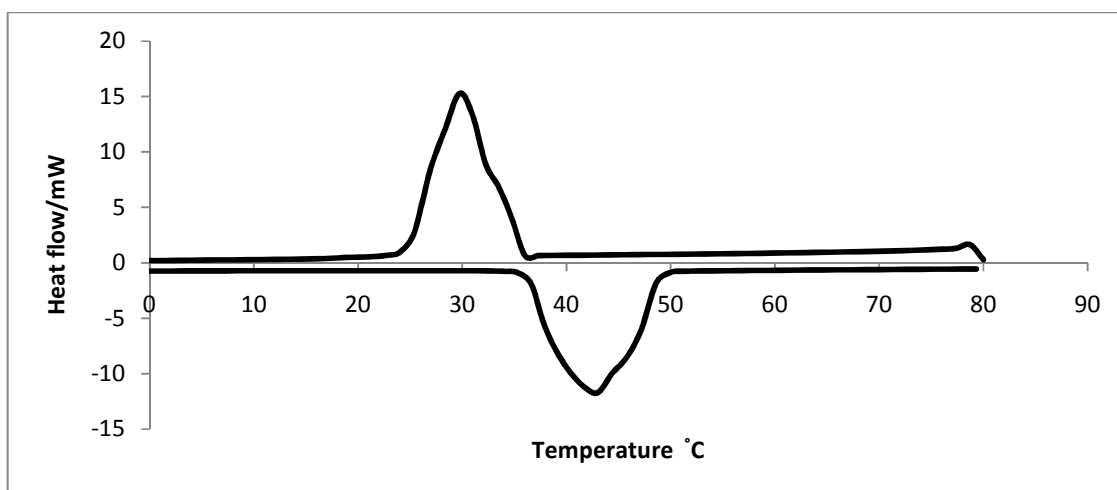
Figure 3.14 DSC curves of encapsulated *N*-eicosane after 200 thermal cycling, *N*-eicosane:polymer (4:1)W/W.

The shape stability of the N-eicosane microcapsule prepared at the PCM to polymer weight ratio of 4:1 after repeated 200 thermal cycling was characterized by SEM analysis as shown in Figure 3.15 that still showed spherical shape.
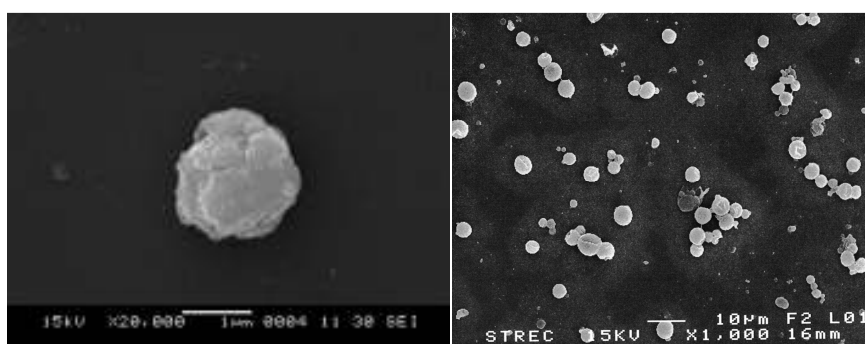

Figure 3.15 SEM image of encapsulated *N*-eicosane after 200 thermal cycling, *N*-eicosane:polymer (4:1)W/W.

3.9 Preparation of Thermo-regulated NR

Preparation of Thermo-regulated NR by mixing the dried encap-PCM

The encapsulated *N*-eicosane at weight ratio 4:1and 10:1 of *N*-eicosane to EC/MC blend, and the encapsulated paraffin at weight ratio 10:1 of paraffin to EC/MC blend were used for the preparation of Thermo-regulated NR. The thermo-regulated NR was prepared at two ratios, 1:1 and 1:2 of NR to encap- PCM by adding the dried encapsulated PCM into 60% DRC NR latex. However, the obtained latex coagulated very quickly and thus the process failed.

Preparation of Thermo-regulated NR by mixing the encap-PCM suspension

The water suspension of the three encap-PCM microspheres (encap-*N*-eicosane 4:1, 10:1 and encap paraffin 10:1) could easily be mixed with the NR latex. The encap-PCM was added to the 60% DRC NR latex. It was prepared at two ratios, 1:1 and 1:2 NR to encap- PCM, calculating by the weight of dry encap-PCM and dry rubber mass. The obtained milky white liquid could be easily poured into a mold. The dry PCM-rubber piece showed good homogeneity when observed by eyes, only at 1:1 NR to encap- PCM. This ratio was used to prepare the PCM-rubber piece for Thermo-regulation test of the PCM-rubber piece. The obtained rubber piece prepared by the ratio of NR to encap- PCM of 1:2 easily cracked into small pieces so it was concluded that the amount of PCM material was high.

The two PCM-rubbers were prepared at the weight ratio 1:1 of NR: Encapsulated *N*-eicosane 4:1 and 10:1. The water suspension of encapsulated *N*-eicosane could easily be mixed with the 60% DRC NR latex to obtain of the latex with 50% (w/w) PCM microspheres content, as calculated using the weight of dry PCM particle and dry rubber mass. The dry PCM-rubber piece showed good homogeneity when observed by eye. In addition, the SEM images of the PCM-rubber clearly indicated an excellent dispersion of the encapsulated *N*-eicosane into EC/MC blend in the rubber matrix (Figure 3.16 A, B). A higher percentage of PCM microspheres in the rubber, such as 70% (w/w), resulted in rubber piece being easily cracked.

The PCM-rubber was prepared at the weight ratio 1:1 of NR: Encapsulated paraffin10:1. The water suspension of encapsulated *N*-eicosane could easily be mixed with the 60% DRC NR latex to obtain of the latex with 50% (w/w) PCM microspheres content, as calculated using the weight of dry PCM particle and dry rubber mass. The dry PCM-rubber piece showed good homogeneity when observed by eye. In addition, the SEM images of the PCM-rubber clearly indicated an excellent dispersion of the encapsulated *N*-eicosane into EC/MC blend in the rubber matrix (Figure 3.16 C). A higher percentage of PCM microspheres in the rubber, such as 70% (w/w), resulted in rubber piece being easily cracked.

3.10 Thermo-regulation test of the PCM-rubber piece

Thermo-regulation property of the PCM-rubber could be observed clearly through a thermal camera. The test was carried out on the circular rubber piece with the radius of 5.2 cm and a thickness of 0.315 cm (containing 7.2 g of the rubber mass and 7.2 g of the encap-C20 mass).

The PCM-rubbers were prepared at the weight ratio 1:1 of NR: Encapsulated N-eicosane 4:1

The thermo-regulation property of the PCM-rubber could be observed clearly through a thermal camera. When the PCM-rubber piece transferred from room temperature (28 °C) onto a heated surface at 50-52 °C, the PCM-rubber piece maintained a temperature of lower than 40 °C for 20 min, compared to the control which reached 50 °C within 9 min (Figure 3.17). Similarly, when the warm PCM-rubber pieces (temperature of 46 °C) were placed on the room temperature surface (28 °C), the PCM-rubber piece could maintain the temperature of over 30 °C for more than 40 min, while the control rubber piece dropped to 29 °C within 15 min (Figure 3.17).

The PCM-rubbers were prepared at the weight ratio 1:1 of NR: Encapsulated N-eicosane 10:1

The thermo-regulation property of the PCM-rubber could be observed clearly through a thermal camera. When the PCM-rubber piece transferred from room temperature (28 °C) onto a heated surface at 50-52 °C, the PCM-rubber could maintain the temperature of lower than 40 °C for 20 min but showed some liquid waxy appearance on surface of the PCM-rubber piece, indicated leakage of the hydrophobic C20 from the microspheres. While the control rubber piece raised temperature to 50 °C within 9 min (Figure 3.18). When the warm PCM-rubber pieces (temperature of 46 °C) were placed on the room temperature surface (28 °C), the PCM-rubber piece could maintain the temperature of over 30° C for more than 40 min, while the control rubber piece dropped to 29 °C within 15 min (Figure 3.18).
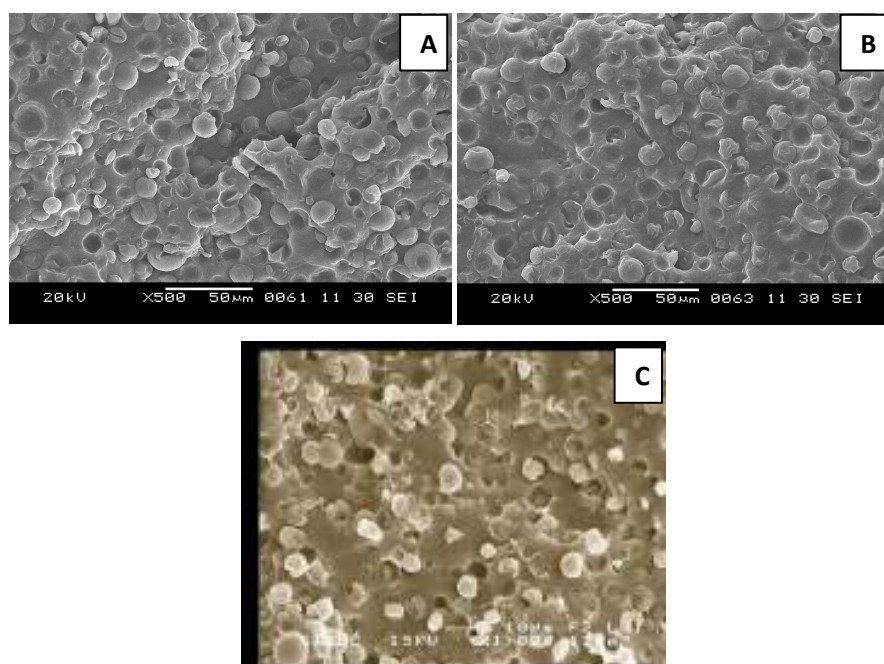
Figure 3.16 SEM image of the PCM-rubber at ratios 1:1 NR to encap- PCM, (A) Encap-*N*-eicosane rubber 4:1, (B) Encap-*N*-eicosane 10:1 rubber, (C) Encap-paraffin 10:1 rubber.
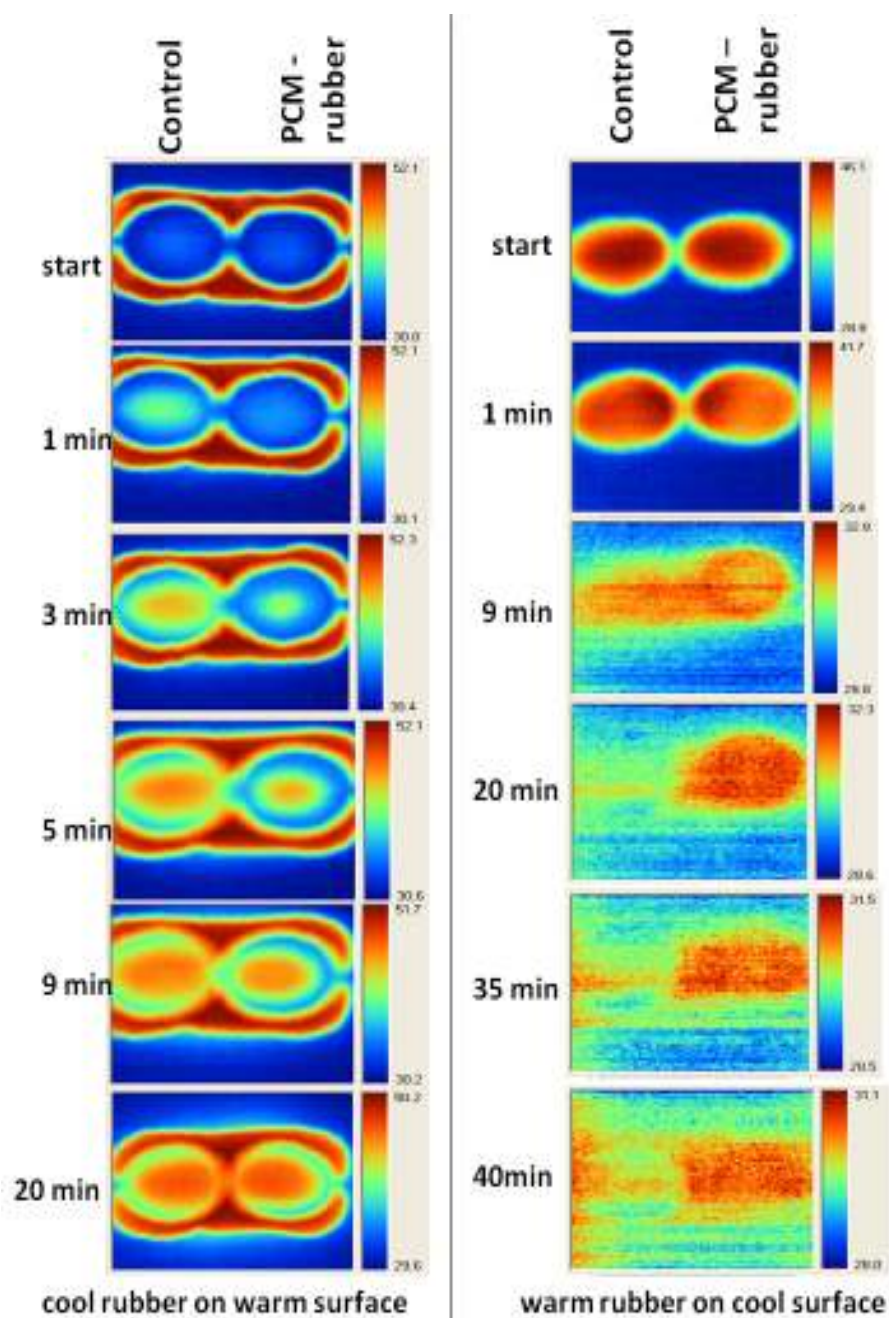
Figure 3.17 Images from thermal camera showing thermo-regulation property of the PCM-rubber at ratios 1:1of NR to Encap-*N*-eicosane 4:1. Left: The cool circular piece of control rubber and that of PCM-rubber were put onto the warm surface (50 °C) and the pictures were taken periodically. Right: The warm rubber pieces were left at room temperature (28 °C) and the pictures were taken periodically.
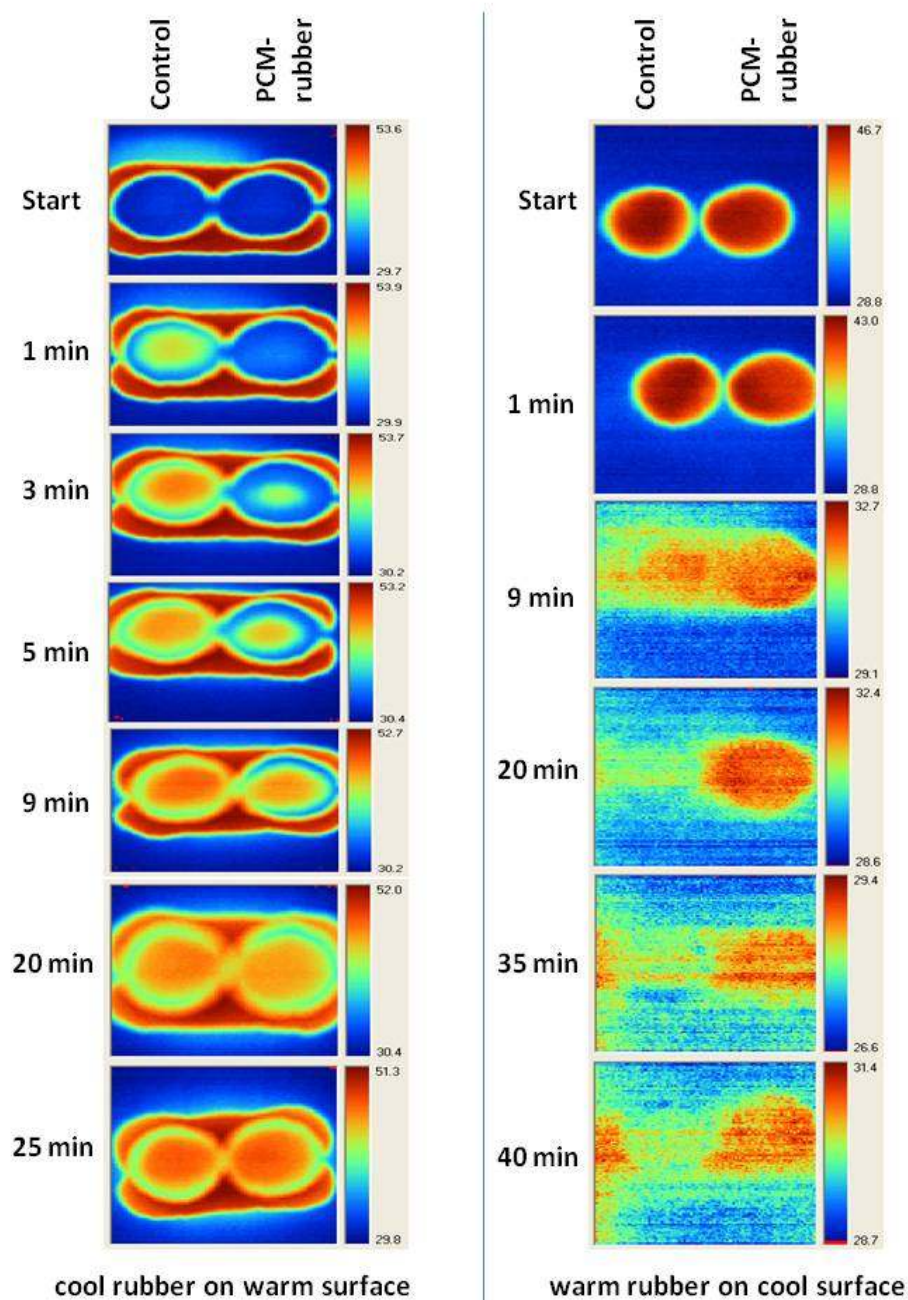
Figure 3.18 Images from thermal camera showing thermo-regulation property of the PCM-rubber at ratios 1:1of NR to Encap-*N*-eicosane 10:1. Left: The cool circular piece of control rubber and that of PCM-rubber were put onto the warm surface (50 °C) and the pictures were taken periodically. Right: The warm rubber pieces were left at room temperature (28 °C) and the pictures were taken periodically.
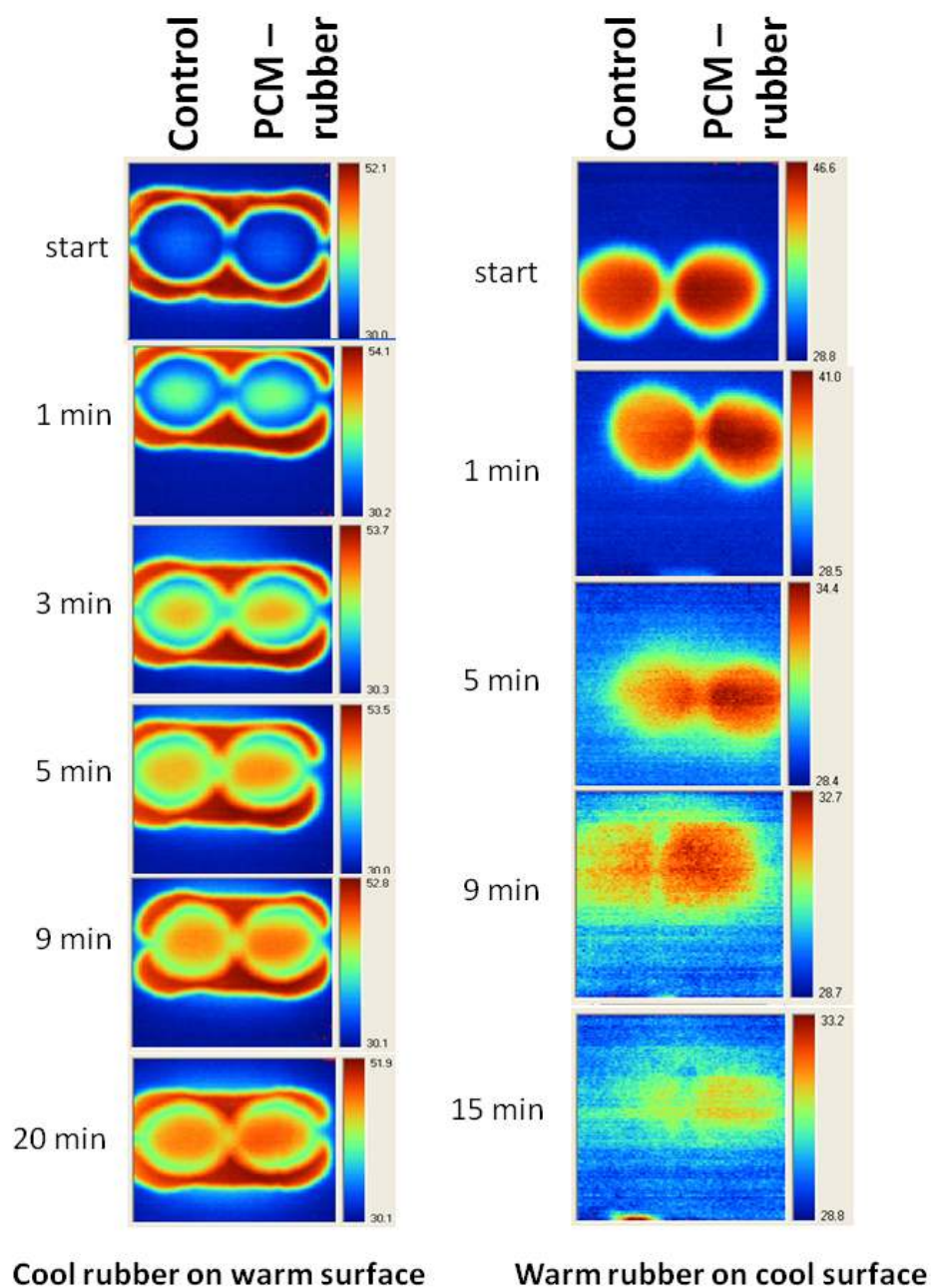
Figure 3.19 Images from thermal camera showing thermo-regulation property of the PCM-rubber at ratios 1:1 of NR to Encap paraffin 10:1. Left: The cool circular piece of control rubber and that of PCM-rubber were put onto the warm surface (50 °C) and the pictures were taken periodically. Right: The warm rubber pieces were left at room temperature (28 °C) and the pictures were taken periodically.

The PCM-rubbers were prepared at the weight ratio 1:1 of NR: Encapsulated paraffin 10:1

The PCM-rubber could be observed clearly through a thermal camera. When the PCM-rubber piece transferred from room temperature (28 °C) onto a heated surface at 50-52 °C, the PCM-rubber piece maintained a temperature of lower than 40 $^{\circ}$C for 5 min, compared to the control which reached 50 $^{\circ}$C within 9 min (Figure 3.19). Similarly, when the warm PCM-rubber pieces (temperature of 46 $^{\circ}$C) were placed on the room temperature surface (28 $^{\circ}$C), the PCM-rubber piece could maintain the temperature of over 30°C for more than 15 min, while the control rubber piece dropped to 29 $^{\circ}$C within 9 min (Figure 3.19).

3.11 Thermal stability test of the PCM microspheres in PCM-rubber piece

The thermal stability test of PCM microspheres in PCM-rubber piece was analyzed by keeping the PCM-rubber piece (diameter of 5.2 cm and thickness of 0.315 cm) in oven at 80 and 100 °C for 20 min in order to check the stability of PCM microspheres in PCM-rubber piece after curing.

The PCM-rubber prepared at 1:1 of NR: Encapsulated *N*-eicosane (4:1) could be kept at 80 °C for 20 min without any evidence of *N*-eicosane leaking out of the rubber piece, as evaluated by the absence of an oily liquid in the rubber piece but kept at 100 °C for 20 min showed the liquid *N*-eicosane leaking out of the rubber piece.

The PCM-rubber at ratios 1:1 NR to Encapsulated *N*-eicosane (10:1) kept at 80 and 100°C for 20 min showed the leakage of liquid *N*-eicosane leaking from the rubber piece.

3.12 Tensile Measurement
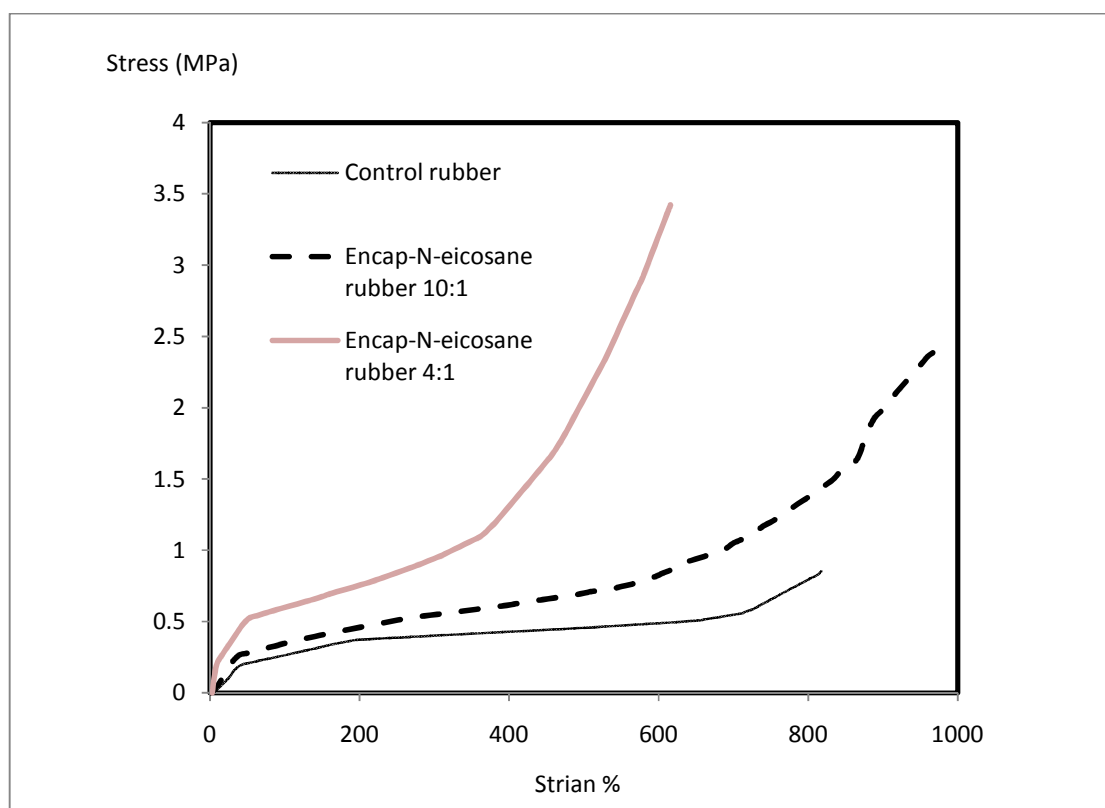
Figure 3.20 Tensile stress-strain curve of the PCM-rubber and the control rubber

The mechanical properties of PCM-rubber and the control rubber are shown in figure 3.20. The modulus at 150% elongation (M_{150}) and tensile strength (T_B) indicated clearly that the two PCM-rubbers possessed an increased tensile strength with the compensation of reduced elongation property, compared to the control rubber. The stress-strain curves of the two PCM-rubbers revealed similar modulus (stress values at a given strain) up to the applied strain of 50 %, but thereafter at higher strain the two PCM-rubbers showed higher stress value. The hardness of the two PCM-rubbers increased when compared to the control rubber with the PCM-rubber at ratios 1:1 NR to Encapsulated *N*-eicosane 4:1 showed higher hardness. This means that the encap- C20 microspheres can be used as filler to not only inherit thermo-regulation property to the rubber but also to improve the mechanical strength of the rubber.

CHAPTER IV

CONCLUSION

We have demonstrated a successful fabrication of *N*-eicosane -loaded microspheres through the simple novel liquid to solid encapsulation process, using EC blend MC as the shell material, to give encap- *N*-eicosane microspheres with increased heat storage capacity, comparing to the capacity of the pure *N*-eicosane,. The best weight ratio between ethylcellulose and methylcellulose was 2:1for the formation of PCM microcapsules. The obtained PCM microspheres contain only biocompatible materials and show good thermo-regulation property.

The encap-C20/EC/MC microspheres with an increased heat storage capacity compared to the capacity of the pure C20. The encap-C20 with the 20% (w/w) polymer content gave 9.93% and 2.89% increase in the absolute enthalpy value during crystallization and melting over that for the unencapsulated C20. The SEM and TEM analysis showed core-shell microspherical architecture and dynamic light scattering analysis gave the agreeable particle sizes of 7.7 ± 5.9 μm, showed good thermal stability after 200 thermal cycling repeating, the average latent heats of melting and freezing were 212.80 J/g and 207.13 J/g, respectively.

A 28.89% and 24.4% increase in the absolute enthalpy value during crystallization and melting were observed for the encap-C20 with the 9% (w/w) polymer content over that of the unencapsulated C20. The SEM and TEM analysis showed core-shell microspherical architecture and dynamic light scattering analysis gave the agreeable particle sizes of 6.8 ± 2.9 μm. The encapsulated paraffin with the 9% (w/w) polymer content showed good absolute enthalpy value but possess poor thermal stability, showed the leakage of the liquid paraffin and could not disperse in water. The SEM and TEM analysis showed the core-shell microspherical architecture, and dynamic light scattering analysis gave agreeable particle sizes of 6.2 ± 2.4 μm.

The encapsulated *N*-eicosane and encapsulated paraffin microcapsules can be used as filler to inherit improved thermo-regulation property of rubber. The thermo-regulated capacity of the PCM rubber depended on PCM component. The C20 microspheres dispersed well in natural rubber latex and produced thermo-regulated rubber with improved mechanical strength.

REFERENCES

[1] Boulard, T., Razafinjohany, E., Baille, A., Jaffrin, A., and Fabre, B. Performance of a greenhouse heating system with a phase change material. <u>Agricultural and Forest Meteorology</u>, *52* (3-4) (1990): 303-318.

[2] Sánchez, P., Sánchez-Fernandez, M. V., Romero, A., Rodríguez, J. F., and Sánchez-Silva, L. Development of thermo-regulating textiles using paraffin wax microcapsules. <u>Thermochimica Acta</u>, *498* (1-2) (2010): 16-21.

[3] Ulfvengren, R. Will PCM help athletes in the Olympic games in Athens 2004. <u>IEA ECES IA Annex 17 6th Workshop</u>, Arvika Sweden, 2004.

[4] Olsson, L. Cooling of newborn baby with PCM. <u>IEA ECES IA Annex 17 6th Workshop</u>, Arvika Sweden, 2004.

[5] Alexiades, V., and Solomon, A.D. Mathematical Modeling of Melting and Freezing Process. Washington DC: Hemisphere Publishing Corporation, 1992.

[6] Barbara, P. Driving more comfortably with phase change materials. <u>Technical Textiles International</u>, 11 (2) (2002): 24–27.

[7] Lane, G.A. Phase Change Thermal Storage Materials. In: Hand Book of Thermal. Washington DC: Hemisphere Publishing Corporation, 1998.

[8] Hale, D.V., Hoover, M.J., and O'Neill, M.J. Phase Change Materials Hand Book. NASA : Marshal Space Flight Center, 1971.

[9] Hasnain, S. Review on sustainable thermal energy storage technologies, part I: heat storage materials and techniques. <u>Energy Conservation and Management</u> 39 (1998): 1127–1138.

[10] Lane, G. A. Solar Heat Storage: Latent Heat Materials. Florida: Boca Raton, Florida, 1983.

[11] Himran, S., Suwono, A., and Mansoori, G. A. Characterization of Alkanes and Paraffin Waxes for Application as Phase Change Energy Storage Medium. Energy Sources, *16* (1) (1994): 117-128.

[12] Fukai, J., Hamada, Y., Morozumi, Y., and Miyatake, O. Effect of carbon-fiber brushes on conductive heat transfer in phase change materials. International Journal of Heat and Mass Transfer, *45* (24) (2002): 4781-4792.

[13] Elgafy, A., and Lafdi, K. Effect of carbon nanofiber additives on thermal behavior of phase change materials. Carbon, *43* (15) (2005): 3067-3074.

[14] Bugaje, I. M. Enhancing the thermal response of latent heat storage systems. International Journal of Energy Research, 21 (1997): 759–766.

[15] S.M, H. Review on sustainable thermal energy storage technologies, Part I: heat storage materials and techniques. Energy Conversion and Management, *39* (11) (1998): 1127-1138.

[16] Sakellariou, P., Rowe, R. C., and White, E. F. The thermomechanical properties and glass transition temperatures of some cellulose derivatives used in film coating. International Journal of Pharmaceutics, *27* (2-3) (1985): 267-277.

[17] Crowley, M. M., Schroeder, B., Fredersdorf, A., Obara, S., Talarico, M., Kucera, S., and McGinity, J. W. Physicochemical properties and mechanism of drug release from ethyl cellulose matrix tablets prepared by direct compression and hot-melt extrusion. International Journal of Pharmaceutics, *269* (2) (2005): 509-522.

[18] Rimdusit, S., Jingjid, S., Damrongsakkul, S., Tiptipakorn, S., and Takeichi, T. Biodegradability and property characterizations of Methyl Cellulose: Effect of nanocompositing and chemical crosslinking. Carbohydrate Polymers, *72* (3) (2008): 444-455.

[19] Muzzarelli, R., and Muzzarelli, C. Chitosan Chemistry: Relevance to the Biomedical Sciences Polysaccharides I., Vol 186 Springer Berlin: Heidelberg, 2005.

[20] Kurita, K. Chitin and chitosan: functional biopolymers from marine crustaceans. Mar Biotechnol (NY), *8* (3) (2006): 203-26.

[21] Harish Prashanth, K. V., and Tharanathan, R. N. Chitin/chitosan: modifications and their unlimited application potential—an overview. Trends in Food Science & Technology, *18* (3) (2007): 117-131.

[22] Pillai, C. K. S., Paul, W., and Sharma, C. Chitin and chitosan polymers: Chemistry, solubility and fiber formation. Progress in Polymer Science, *34* (7) (2009): 641-678.

[23] Ravindra, R., Krovvidi, K. R., and Khan, A. A. Solubility parameter of chitin and chitosan. Carbohydrate Polymers, *36* (2-3) (1998): 121-127.

[24] Wang, J., Jin, X., and Chang, D. Chemical modification of chitosan under high-intensity ultrasound and properties of chitosan derivatives. Carbohydrate Polymers, *78* (1) (2009): 175-177.

[25] Rodgers, B. Rubber compounding: Chemistry and applications. New York: Marcel Dekker, 2004.

[26] Gazeley, F., Gorton, A. T., and Pendle, T. D. Natural rubber science and technology. Latex concentrates: Properties and composition. New York: Oxford University Press. 1988.

[27] Cabeza, L.F., Roca, J., Nogues, M., Zalba, B., and Marin, J.M. Transportation and conservation of temperature sensitive materials with phase change materials: state of the art. IEA ECES IA Annex 17. 2nd Workshop. Ljubljana Slovenia, 2002.

[28] Vasiliev, L. L., Burak, V. S., Kulakov, A. G., Mishkinis, D. A., and Bohan, P. V. Latent heat storage modules for preheating internal combustion engines: application to a bus petrol engine. Applied Thermal Engineering, *20* (10) (2000): 913-923.

[29] Tan, F. L., and Tso, C. P. Cooling of mobile electronic devices using phase change materials. Applied Thermal Engineering, *24* (2-3) (2004): 159-169.

[30] Koschenz, M., and Lehmann, B. Development of a thermally activated ceiling panel with PCM for application in lightweight and retrofitted buildings. <u>Energy and Buildings</u>**, ***36* (6) (2004): 567-578.

[31] Zhang, X., Fan, Y., Tao, X., and Yick, K. Crystallization and prevention of supercooling of microencapsulated n-alkanes. <u>Journal of Colloid and Interface Science</u>**, ***281* (2) (2005): 299-306.

[32] Wang, W., Yang, X., Fang, Y., and Ding, J. Preparation and performance of form-stable polyethylene glycol/silicon dioxide composites as solid–liquid phase change materials. <u>Applied Energy</u>**, ***86* (2) (2009): 170-174.

[33] Fang, G., Li, H., Yang, F., Liu, X., and Wu, S. Preparation and characterization of nano-encapsulated n-tetradecane as phase change material for thermal energy storage. <u>Chemical Engineering Journal</u>**, ***153* (1-3) (2009): 217-221.

[34] Deveci, S., and Basal, G. Preparation of PCM microcapsules by complex coacervation of silk fibroin and chitosan. <u>Colloid & Polymer Science</u>**, ***287* (12) (2009): 1455-1467.

[35] Alkan, C., Sarı, A., and Karaipekli, A. Preparation, thermal properties and thermal reliability of microencapsulated n-eicosane as novel phase change material for thermal energy storage. <u>Energy Conversion and Management</u>**, ***52* (1) (2011): 687-692.

[36] Sarı, A., Alkan, C., and Karaipekli, A. Preparation, characterization and thermal properties of PMMA/n-heptadecane microcapsules as novel solid–liquid microPCM for thermal energy storage. <u>Applied Energy</u>**, ***87* (5) (2010): 1529-1534.

[37] Sánchez, P., Sánchez-Fernandez, M. V., Romero, A., Rodríguez, J. F., and Sánchez-Silva, L. Development of thermo-regulating textiles using paraffin wax microcapsules. <u>Thermochimica Acta</u>**, ***498* (1-2) (2010): 16-21.

[38] Müller, R. H., Jacobs, C., and Kayser, O. Nanosuspensions as particulate drug formulations in therapy: Rationale for development and what we can expect for the future. Advanced Drug Delivery Reviews, *47* (1) (2001): 3-19.

[39] Montenegro, R., and Landfester, K. Metastable and Stable Morphologies during Crystallization of Alkanes in Miniemulsion Droplets. Langmuir, *19* (15) (2003): 5996-6003.

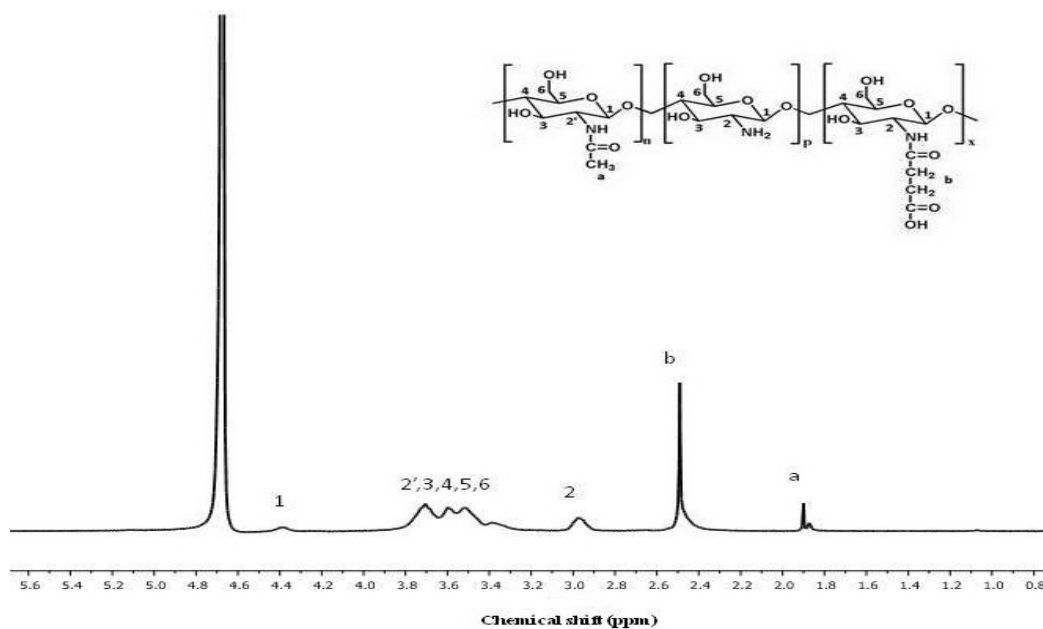APPENDICES

1. Determination of degree of succinyl substitution

Figure A1. ^{1}H NMR spectrum of *N*-succinylchitosan1 (N-SCS1)

The degree of grafting could be determined using equation (1):

$$DG = \frac{I_{graft} \times DD}{n \times I_{cs}}$$

(1)

I_{graft} = the intensity of grafted moiety

DD = the amount of deacetylation degree

n = number of protons of grafted moiety

I_{cs} = the intensity of hydrogen atom of chitosan's glucosamine unit

From the ^{1}H NMR spectrum (Figure A1), using the integral ratio between 4H from ethyl group of succinyl (2.42-2.50 ppm) and 1H from C2 of glucosamine unit (at 2.98 ppm) with 85% deacetylation degree:

$$DG = \frac{2.02 \times 0.85}{4 \times 1}$$

$$DG = 0.43$$

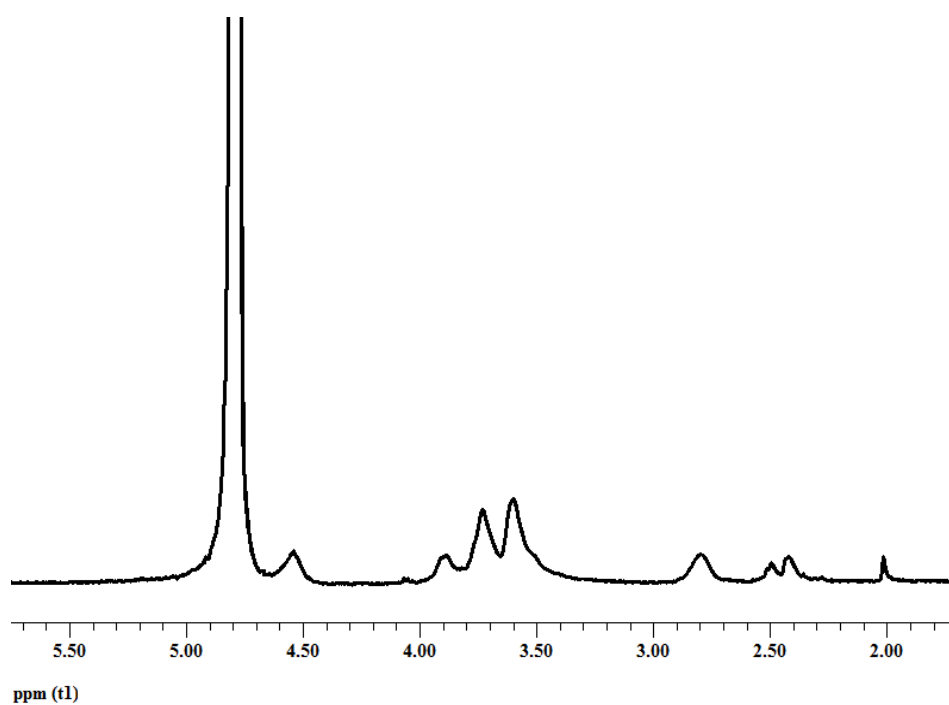The degree of succinyl substitution could be estimated as 0.43.

Figure A2. ^{1}H NMR spectrum of *N*-succinylchitosan2 (N-SCS2)

The degree of grafting could be determined using equation (1):

$$DG = \frac{I_{graft} \times DD}{n \times I_{cs}}$$

(1)

I_{graft} = the intensity of grafted moiety

DD = the amount of deacetylation degree

n = number of protons of grafted moiety

I_{cs} = the intensity of hydrogen atom of chitosan's glucosamine unit

From the ^{1}H NMR spectrum (Figure A1), using the integral ratio between 4H from ethyl group of succinyl (2.42-2.50 ppm) and 1H from C2 of glucosamine unit (at 2.98 ppm) with 85% deacetylation degree:

$$DG = \frac{1.13 \times 0.85}{4 \times 1}$$

$$DG = 0.24$$

The degree of succinyl substitution could be estimated as 0.24.

VITAE

Mr. Songpon Phadungphatthanakoon was born on November 24, 1986 in Burirum, Thailand. He has got Bachelor's Degree of Science in Chemistry (second class honor) from Srinakharinwirot University in 2008. And then, he started his graduate study a Master's degree in the Program of Organic chemistry, Faculty of Science, Chulalongkorn University. During master study, he had a great opportunity to presented his work in poster session in the topic of "Encapsulation N-eicosane as phase change" at the The 14th Asian Chemical Congress (14th ACC). The finance for joining the conference was supported by National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials (NCE-PPAM) and the Graduate School, Chulalongkorn University.

His present address is 169 Moo 11 Chumhed, Muang, Buriram Thailand 31000.