PREPARATION AND CHARACTERIZATION OF DIVINYLBENZENE-BASED CAPSULE ENCAPSULATED OCTADECANE: MONOMER DROPLET GENERATED BY PHASE INVERSION EMULSIFICATION

MD. ZAHIDUL ISLAM

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE PROGRAM IN INNOVATIVE CHEMISTRY

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Name – Surname	Mr. Md. Zahidul Islam
Program	Innovative Chemistry
Thesis Advisor	Assistant Professor Preeyaporn Chaiyasat, Ph.D.
Academic Year	2013

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Date 4 Month April Year 2014

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ABSTRACT

This research was aimed to study the preparation of poly(divinylbenzene)-/octadecane (PDVB/OD) and poly(divinylbenzene-methylmethacrylate)/octadecane (P(DVB-MMA)/OD) microcapsules by microsuspension polymerization using phase inversion emulsification (PIE) for monomer droplet generation.

In the first step, PDVB/OD microcapsule was prepared using PIE for the oil droplets generation. The influence of the surfactant type and amount with and without co-surfactant on the colloidal stability, particle size and size distribution of microcapsules were investigated compared with the conventional emulsification technique. In the case of PIE, the microcapsules size about 1.5 μm with narrow particle size distribution (PSD) and good colloidal stability throughout the polymerization were obtained using polyvinyl alcohol and sodium dodecyl sulphate as the surfactant and cosurfactant, respectively. On the other hand, the coagulation was observed using conventional technique with the same recipe of PIE. In the second step, MMA was introduced to the copolymer microcapsule to improve the latent heats of the encapsulated OD. The influence of the additional rate of the aqueous phase and the monomer ratio were studied. At the additional rate of 2 mL/min, approximately 4 μm microcapsule with narrower PSD and higher colloidal stability than the other conditions were obtained. The increase of MMA content from 50 to 70 wt % increased latent heats of the encapsulated OD due to high phase separation of P(DVB-MMA) shell and OD core.

From the results, it can be concluded that PDVB/OD and P(DVB-MMA)/OD microcapsules were successfully prepared by microsuspension polymerization using PIE for oil droplet generation.

Keywords: Octadecane, Microcapsule, Microsuspension polymerization, Phase inversion emulsification

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Md. Zahidul Islam

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List of Abbreviations

PCM	Phase Change Material
PIE	Phase Inversion Emulsification
PSD	Particle Size Distribution
DVB	Divinylbenzene
MMA	Methyl Methacrylate
OD	Octadecane
PVA	Polyvinyl Alcohol
Tween80	Polyoxyethylene Sorbitan Monooleate
BPO	Benzoyl Peroxide
SDS	Sodium Dodecyl Sulfate
$NaNO_2$	Sodium nitrite
DSL	Dynamic Light Scattering
DSC	Differential Scanning Calorimetry
TGA	Thermo Gravimetric Analysis
OM	Optical Microscopy
SEM	Scanning Electron Microscopy

CHAPTER 1
INTRODUCTION

1.1 Important and background of thesis

Heat storage or phase change materials (PCMs) are attractive for many industrial applications such as air condition of building, solar heat storage, thermal adaptable fibers and temperature-adaptable greenhouses [1-5]. Among of PCMs, paraffin wax is one of the most attractive PCMs because of a wide range of melting and crystallization temperatures. Paraffin wax has moderate energy capacity, nontoxic, non-corrosive and also chemically inert. However, its thermal conductivity is low which limits the application. To overcome this drawback, a large surface area is required. Therefore, in recent years, the encapsulation of paraffin wax has been developed to provide large heat transfer area. Moreover, it also controls the volume change of the storage materials as phase changes occurs and protect the influence from the outside environment [6].

There are many encapsulation techniques. The encapsulation by monomer polymerization using internal phase separation mechanism [7] is one of the most famous techniques especially suspension and miniemulsion polymerizations. They are environmental friendly polymerization techniques in aqueous dispersed systems. Both polymerizations are carried out in oil droplets where PCMs, monomer and initiator are completely dissolved and dispersed in the continuous phase of surfactant aqueous solution. When the polymerization is initiated by existing initiator, the polymer chains gradually move to the interface of the droplet forming the outer shell while more hydrophobic materials as PCMs locate inside as the capsule core. Then, by these techniques, high encapsulation efficiency is always obtained. However, both polymerizations generally need high shear rate to generate the oil droplets leading to high cost and energy consumption. Therefore, they are not appropriate for the industrial application. Moreover, microcapsules with broad particle size distribution (PSD) are also obtained in the case of the conventional suspension polymerization. From our previous works, we have successfully prepared polydivinylbenzene (PDVB)/OD microcapsules [8-10] by microsuspension polymerization of DVB/OD droplets

produced by homogenization. However, they were polydispersed of particle size resulting in a wide range of thermal properties especially crystallization temperature (T_c) of the encapsulated OD. There is some research works reported the generation of monomer droplets using only mechanical stirring (approximately 800-2000 rpm). It was named as suspensionlike polymerization [11-17] for the preparation of microcapsules. However, the obtained microcapsules were still quite broad PSD. There are many techniques used for the preparation of narrow PSD oil droplets. The shirazu porous glass (SPG) membrane emulsification was used for the preparation of comparatively monodisperse DVB/HD droplets [18]. It was also used for the preparation of DVB and acrylic monomer with HD droplets [19]. In addition, the microfluidic technique was also used for the preparation of monodisperse submicron-sized drops [20]. However, special equipments and long time were required in all techniques. Therefore, to overcome these disadvantages, the utilization of low energy method with a simple instrument such as phase inversion emulsification (PIE) to prepare the narrow PSD oil droplets is interesting.

1.2 Objectives of thesis

1.2.1 To prepare PDVB/OD and P(DVB-MMA)/OD with narrow PSD by micro- suspension polymerization using PIE for monomer droplet generation compared with the conventional method

1.2.2 To characterize the properties of the prepared microcapsules

1.3 Scope of thesis

1.3.1 Study the preparation of PDVB/OD and P(DVB-MMA)/OD microcapsules by microsuspension polymerization of monomer(s)-OD droplets prepared by PIE and conventional method

1.3.2 Characterize the prepared microcapsules in terms of morphology, particle size and distribution and thermal properties

1.4 The concept of thesis

To prepare narrow PSD monomer/PCM droplets using low energy technique, PIE was then applied. In food chemistry, instead of the conventional emulsification using high-shearing, high-pressure homogenization or ultrasound generation, nano- and micro- emulsions have successfully prepared using PIE methods. Recently, PIE is successfully applied for the generation of oil droplets in miniemulsion polymerization to prepare nanopolymer particles with narrow PSD [21-26]. Generally, the generated oil droplets are stabilized by surfactant formed at the oil-water interface on drop wise addition of the continuous phase into the dispersed phase. This technique may reduce oil droplets coalescence compared with the conventional technique which surfactant is pre-dissolved in water. It is because of higher rate of surfactant adsorption on the oil-water interface in the case of PIE than the diffusion rate from the aqueous phase to the droplet interface. Then, it is interesting to implement PIE for monomer droplet generation in microsuspension polymerization for the preparation of microencapsulated PCMs having narrow PSD.

Therefore, the utilization of PIE for oil droplets generations were studied to prepare narrow PSD DVB-based microcapsules by microsuspension polymerization based on the optimum condition of our previous works [8-10] (monomer/PCMs ratio, initiator content and polymerization temperature). In this work, OD, a kind of paraffin wax, was selected to be use as a PCM. The influence of surfactant types and amounts (with and without co-surfactant), the aqueous phase additional rate and the copolymerization with more hydrophilic monomer as methyl methacrylate (MMA) on the colloidal stability, particle size and PSD of the microcapsules were investigated. Moreover, the thermal properties of the microencapsulated OD were also determined.

1.5 Expectations of thesis

1.5.1 To obtain the optimum condition for the preparation of PDVB/OD and P(DVB-MMA)/OD microcapsules by microsuspension polymerization

1.5.2 To obtain the microcapsules having narrow PSD using low energy technique as PIE for monomer(s)-OD droplets generation

CHAPTER 2
DOCUMENTS AND LITERATURES

2.1 Phase Change Materials

PCMs or heat storage materials are the materials that can store and release energy above their phase transition temperatures. PCMs are one of the most efficient ways of storing thermal energy. The latent heat storage method provides much higher storage density with a smaller temperature difference between storing and releasing heat than the others. The PCMs used for thermal storage systems should exhibit desirable thermo physical, kinetics and chemical properties. For thermal properties, they should have suitable phase transition temperature with the working temperature, high latent heat of transition and good heat transfer. Their appropriate physical properties are favourable phase equilibrium during freezing-melting of heat storage, high density to allow a smaller size of storage container, small volume change and low vapor pressure. For kinetic properties, no supercooling with sufficient crystallization rate is also important. Moreover, they should be long-term chemical stable, compatible with materials of construction, no toxicity and no fire hazard. PCMs must be non-toxic, non-flammable and non-explosive for safety [27, 28].

2.2 Classification of PCMs

The classification of PCMs is shown in Fig. 2.1 as organic, inorganic and eutectic materials. Normally, inorganic and organic compounds have much different in thermal and chemical behaviours. The properties of each subgroup are discussed in detail below.

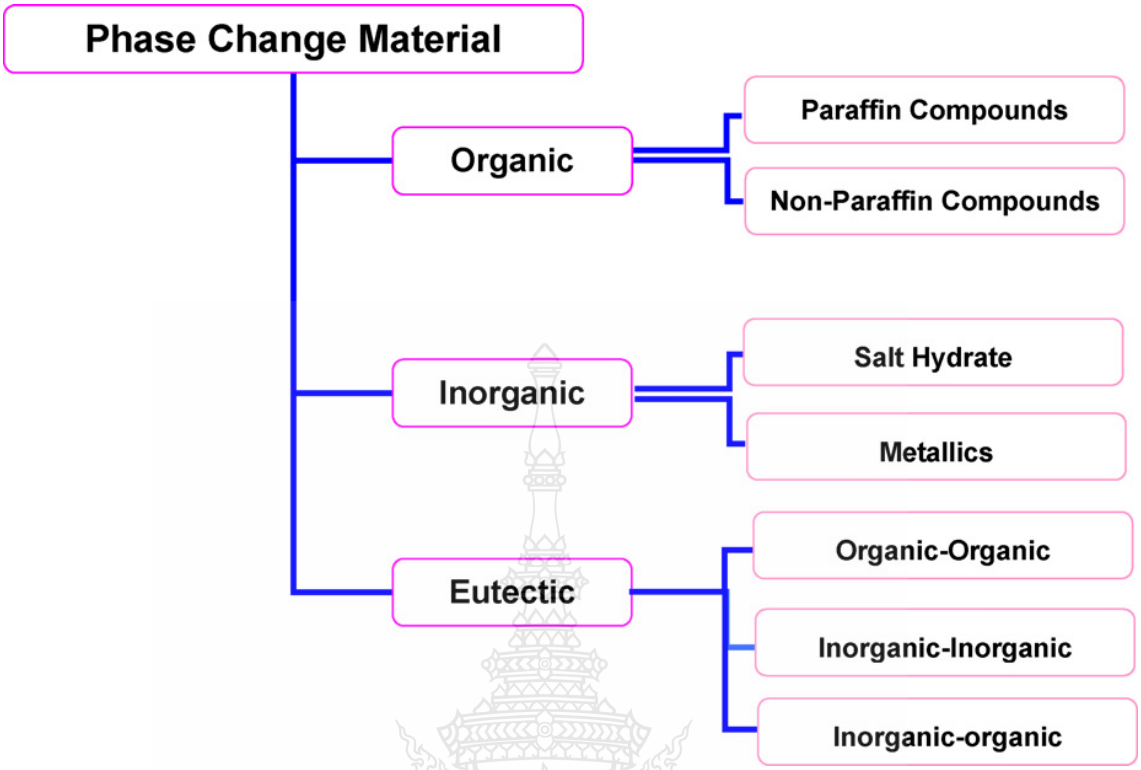


Figure 2.1 Classifications of PCMs [29]

2.2.1 Organic compounds

Organic PCMs are divided into two types, paraffins and nonparaffins.

2.2.1.1 Paraffins

Paraffins or paraffin waxes are alkane that contains carbon and hydrogen with only single bond such as hexadecane ($C_{16}H_{34}$), octadecane ($C_{18}H_{38}$) and nonadecane ($C_{19}H_{40}$). The general chemical structure is $C_n H_{2n+2}$. Normally, they have 3 structures which are linear (normal), branch (iso) and cyclic. If the carbon chain length is increased, the melting point and latent heat of fusion are also increased. Paraffins have many advantages such as low cost, wide temperature range, environmental friendly, non-corrosive and chemically inert. Paraffin waxes have moderate thermal energy storage, a small volume change and low vapor pressure in the melted form. However, only technical grade paraffins are used as PCMs in latent heat storage systems. Paraffins have some disadvantages such as low thermal conductivity,

non-compatibility with the plastic container and moderate flammability [30]. Table 2.1 shows paraffins properties with their melting point and latent heat of fusion.

Table 2.1 Melting point and latent heat of fusion of paraffins [31]

Number of carbon atom	Melting point (°C)	Latent heat of fusion (kJ/Kg)
14	5.5	228
15	10	205
16	16.7	237.1
17	21.7	213
18	28.0	244
19	32.0	222
20	36.7	246
21	40.2	200
22	44.0	249
23	47.5	232
24	50.6	255
25	49.4	238
26	56.3	256
27	58.8	236
28	61.6	253
29	63.4	240
30	65.4	251
31	68.0	242
32	69.5	170
33	73.9	268
34	75.9	269

2.2.1.2 Non-paraffins

There are numerous number of non-paraffin organic PCMs with various properties such as ester, fatty acid, alcohol and glycol. They have their own properties unlike the paraffins which have very similar properties. They are divided into

subgroups as fatty acids and other non-paraffin organic compounds such as polyethylene glycol. Their important properties are high heat of fusion, inflammability, low thermal conductivity, low flash point, varying level of toxicity and instability at high temperatures. Fatty acids have high heat of fusion values compared with that of paraffins. Fatty acids also show reproducible melting and freezing with no supercooling [32]. The fatty acid structure is given by $CH_3(CH_2)_{2n}COOH$. Their major drawback is higher cost about 2-2.5 times than that of technical grade paraffins.

2.2.2 Inorganic compounds

There are two types of inorganic PCMs, salt hydrates and metallics. These PCMs have many advantages such as high heat of fusion, high thermal conductivity, low volume change and availability in low cost [33].

2.2.2.1 Salt hydrates

Salt hydrates are inorganic salts with water forming a typical crystalline solid of general formula $AB.nH_2O$ such as $K_2HPO_4.6H_2O$, $FeBr_3.6H_2O$, $Mn(NO_3)_2.6H_2O$ and $CaCl_2.12H_2O$. The solid-liquid transformation of salt hydrates is a dehydration or hydration of the salt. This process resembles melting or freezing thermodynamically.

In melting process, the hydrate crystals are broken up into anhydrous salt and water. Most of salt hydrates have one problem about incongruent melting due to the release of water of crystallization is not sufficient to dissolve all of the solid phase present. They also have poor nucleating properties resulting in supercooling of the liquid before crystallization. However, to overcome this problem, a nucleating agent is added to provide the nucleation. The attractive properties of salt hydrates are high latent heat of fusion per unit volume, relatively high thermal conductivity (almost double of the paraffins) and small volume change on melting. They are also not corrosive, compatible with plastics and slightly toxic [34].

2.2.2.2 Metallics

Metallics include the low melting metals and metal eutectics. They have high thermal conductivity different from the other PCMs. Table 2.2 is a given selected metallics. These materials have low heat of fusion per unit weight, high thermal conductivity, low specific heat and relatively low vapor pressure [35].

Table 2.2 Melting point and latent heat of fusion of metallics [35]

Material	Melting point (°C)	Latent heat (kJ/kg)
Gallium-gallium antimony eutectic	29.8	-
Gallium	30.0	80.3
Cerrolow eutectic	58	90.9
Bi-Cd-In eutectic	61	25
Cerrobend eutectic	70	32.6
Bi-Pb-In eutectic	70	29
Bi-In eutectic	72	25
Bi-Pb-tin eutectic	96	-
Bi-Pb eutectic	125	-

2.2.3 Eutectics

Eutectic is a minimum-melting composition of two or more components. Every melts and freezes congruently form a mixture of the component crystals during crystallization [36]. Eutectic is melted and froze without segregation. Eutectic materials are organic compounds such as waxes, vegetable oil, sugar, fatty acids and alcohol and salt-based solutions such as glauber's salt, organic salts (acetate/formate based), inorganic salts (chloride/nitrate based) and molten salts.

2.3 Microencapsulation of PCMs

Microencapsulation is a process for envelop solid particles, liquid droplets or gas bubbles as core material with shell material such as polymer or copolymer. This core-shell material is called microcapsule. The microcapsule is particle with average diameter between 1-1000 μm. The particle smaller than 1μm is called nanocapsules where as particle larger than 1000 μm is called macrocapsule [37]. The shell materials of capsules are a wide variety of materials including natural and synthetic polymers depending on the chemical characteristics and intended use of the core [38]. The microcapsule morphology depends on the core material properties and the deposition process of the shell. Microcapsules have both regular and irregular shapes. They are classified as (i) mononuclear type, (ii) polynuclear type and (iii) matrix type on the basis of their morphology. Mononuclear type microcapsules contain the shell around the core called core-shell structure. Polynuclear capsules consist of many cores enclosed within the shell while matrix type capsules are the core material is distributed homogeneously into the shell material in the case of matrix type. In addition to these three morphologies, microcapsules can be mononuclear with multiple shells and clusters of microcapsules [39]. The main advantages of microencapsulation are protection of unstable or sensitive materials from their environments, shelf-life enhancement by preventing the degradation reactions and evaporation and convenient handling of core materials. The characteristics of microcapsule are defined with various parameters such as the particle size, the thickness and impermeability of capsule walls, the mechanical strength of capsule walls to withstand normal handling forces, the durability of capsule walls to temperature, humidity and various solvents, the functionality over numerous phase transition cycles, the good thermal conductivity with increasing heat-transfer area, the resistance to thermal stress for the whole product life, and low cost [40, 41].

The microencapsulation techniques have been developed for many years. They are classified as physical and mechanical methods, chemical method and physicochemical methods [44]. Physical and mechanical processes of microencapsulation are spray-drying, fluidized bed and centrifugal extrusion processes. The chemical processes suitable for microencapsulation are in situ polymerization, interfacial polymerization and microsuspension polymerization. The microencapsula-

tion by physicochemical processes includes simple or complex coacervation. The use of some techniques has been limited to the high cost of processing, regulatory affairs, and the use of organic solvents, which are a concern for health and the environment [45, 46]. Among of them, microsuspension polymerization is one of the most famous techniques for microencapsulation. Microsuspension polymerization is a heterogeneous polymerization system. The polymerization system consists of water-insoluble monomer (s) and oil-soluble initiator dispersed in the continuous aqueous phase having small amount of stabilizer by high shear rate forming the monomer droplets. The mechanical stirring is maintained while the monomer droplets are slowly converted to polymer particles. Polymerization is mainly taken place in the droplets. Usually, suspension polymerization requires the addition of small amounts of a stabilizer to prevent coalescence of the droplets during polymerization. The particle size distribution of the initial monomer droplets and also the formed polymer particles depends on the balance between droplet break-up and droplet coalescence. The particle sizes are in the range of 1-1000 μm. For microsuspension polymerization, the particle sizes are only in the range of 1-100 μm. When the core material is added in oil phase of monomer and initiator mixture, the microcapsules are formed mainly by internal phase separation mechanism.

In the case of microencapsulation using an internal phase separation mechanism, Self-assembling of Phase Separated Polymer method (SaPSeP method) [47, 48] based on an environmentally friendly technique in aqueous dispersed systems is one of the most famous methods. Firstly, monomer (s), core material and oil-soluble initiator are homogeneously dissolved. The mixture is poured in an aqueous solution of surfactant and then stirred with high shear rate to form the monomer droplets. After the polymerization is started at the appropriate temperature, polymer chains are gradually formed until reach the critical chain length, phase separation occurs. Polymer chains move to the droplet interface and form polymer shell encapsulated the core material. The properties of polymer shell and core material such as hydrophilicity and also internal viscosity during polymerization are the main important factors in this method. Some of micro- and nanoencapsulated PCMs were successfully produced by

microsuspension and miniemulsion polymerizations, respectively, with various kinds of polymer shells and paraffin waxes using this SaPSeP method [8].

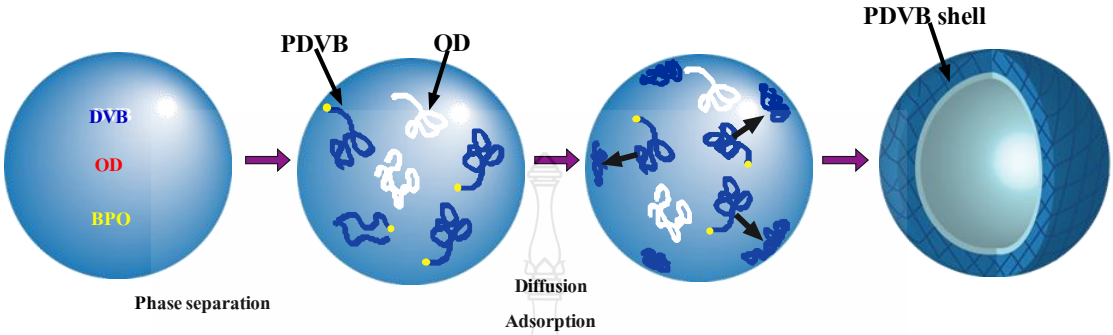


Figure 2.2 Schematic of the Self-assembling of Phase Separated Polymer (SaPSeP) method for the preparation of polydivinylbenzene/octadecane microcapsules [47, 48]

However, the preparation of monomer droplets in microsuspension polymerization normally used high shear rate resulting in high cost and large energy consumption and also broad PSD droplets. Previously, we have successfully prepared the microcapsules of PDVB/OD by suspension polymerization using homogenizer as shown in Fig. 2.3 [49].

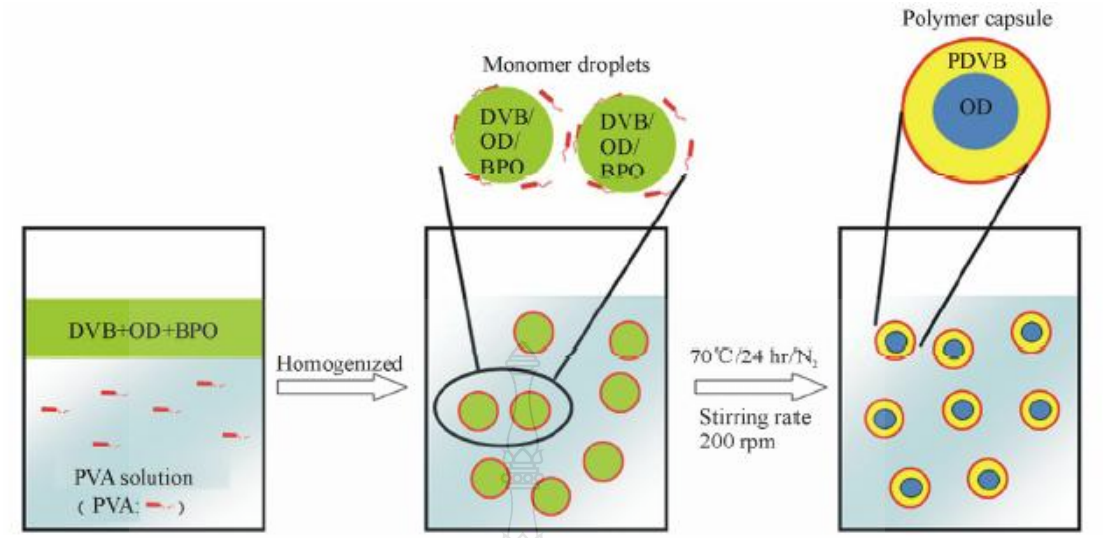


Figure 2.3 Schematic of the preparation process of PDVB/OD microcapsules by microsuspension polymerization [49]

The scanning electron (SEM) and optical (OM) micrographs of the obtained microcapsules are shown in Fig. 2.4. The microcapsule sizes are too polydisperse which affected on the encapsulated OD thermal properties.

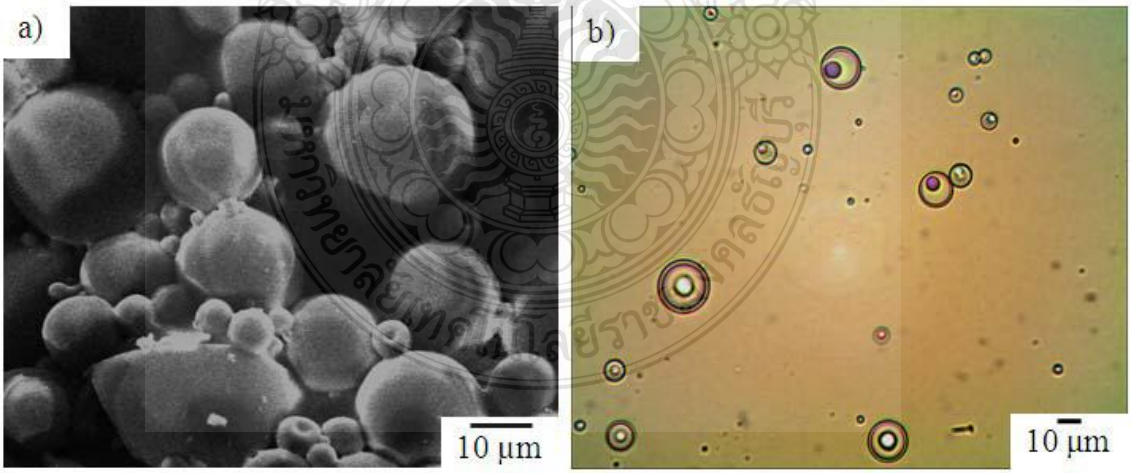


Figure 2.4 SEM (a) and optical (b) micrographs of PDVB/OD microcapsules prepared by microsuspension polymerization [49]

To overcome this disadvantage, recently, some studies reported the generation of monomer droplets using only mechanical stirring (approximately, 800-2000 rpm) called suspension-like polymerization. L. Sanchez-Silva et al. [50] prepared microcapsules of polystyrene encapsulating a commercial type paraffin wax (Repsol YPF) by a suspension-like polymerization. It was carried out at different stirring rates from 600 rpm to 1600 rpm at 108 °C for 6 h under N_2 atmosphere. They also carried out the scale-up microencapsulation process in a pilot plant with the aim of preparing microcapsules with a similar particle size and same PCM content as those observed in the lab-scale. The differences were average particle size and encapsulated paraffin content between two scales at higher stirring rates. Environmental scanning electron microscope (ESEM) micrographs of microcapsules containing paraffin wax synthesized on the laboratory and pilot plant scales were shown in Fig. 2.5 [50]. Using this technique, the microcapsules are successfully prepared but polydispersed particles were still obtained.

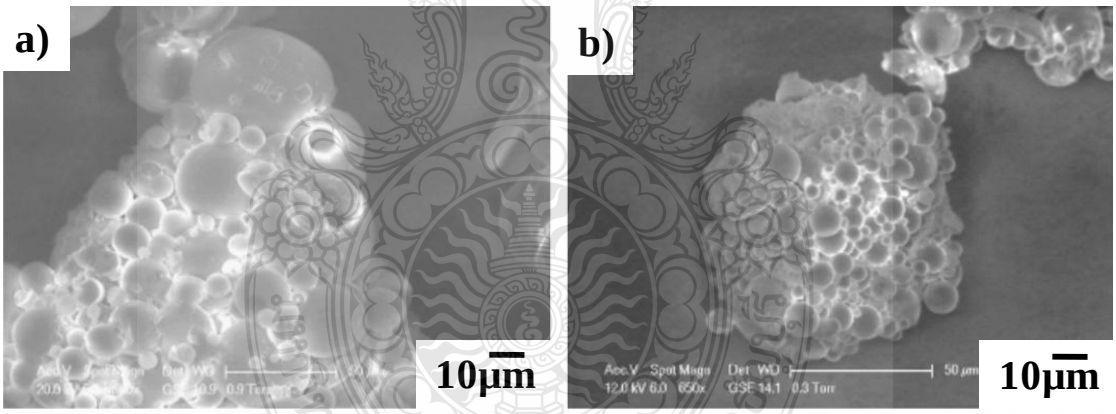


Figure 2.5 ESEM micrographs of microcapsules containing paraffin wax synthesized on (a) the laboratory and (b) the pilot plant scales [50]

2.4 Phase Inversion Emulsification

PIE is widely used in the fabrication of cosmetic products, pharmaceutical products, foodstuff and detergents [51]. The main concept of PIE is that an aqueous phase is gradually dropped into an oil phase in which a surfactant is initially dissolved. Firstly, water in oil (W/O) emulsion is formed [52]. The rate of water droplet coalescence increases as the water amount in the emulsion increases. After that, water is continuously added until the water amount is higher than the oil phase, the W/O emulsion irreversibly inverses to an oil in water (O/W) emulsion called phase inversion as shown in Fig. 2.6 [53]. The rate of surfactant adsorption at the oil interface is higher than that of the conventional technique (using surfactant in aqueous medium). Then, it effectively stabilizes oil droplets resulting in narrow PSD droplets.

From the literature review, PIE is one of the simplest techniques that can be applied for the preparation of oil droplets without high share rate [54]. This technique has many advantages such as low energy consumption, simple technique and narrow PSD droplets formation. Therefore, in this work, PIE is firstly applied for narrow PSD microcapsules preparation.

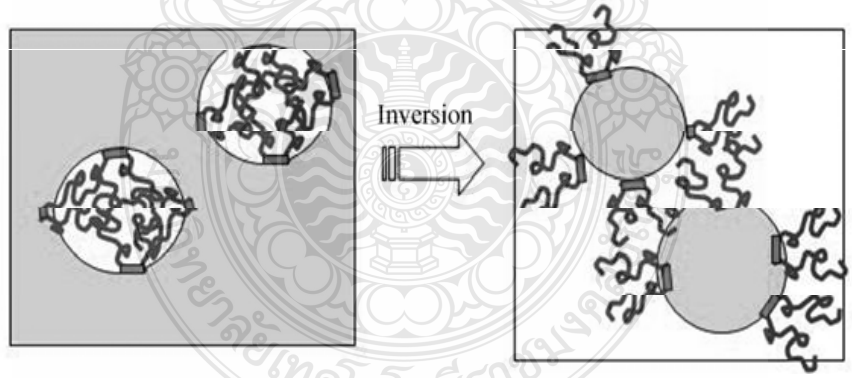


Figure 2.6 Schematic view of the inversion of PIE from W/O to O/W emulsion [53]

By this process, long term stable emulsions characterized by very small average diameter and narrow PSD are obtained. Figure 2.7 showed an OM of the final emulsion and the droplet size distribution.

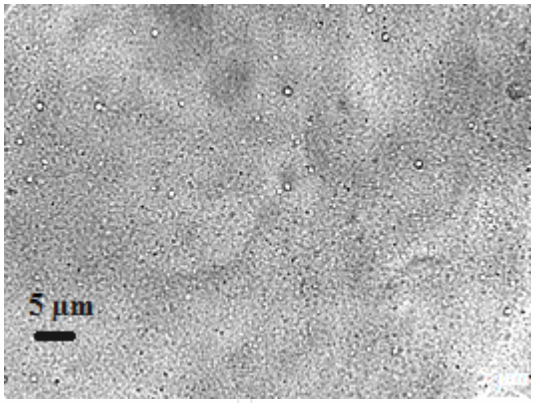


Figure 2.7 OM image of the final emulsion [55]

CHAPTER 3
EXPERTMENTAL PART

3.1 Chemicals and instruments

3.1.1 Chemicals

Name	Grade	Brand
1. Divinylbenzene (DVB)	Technical, 80%	Sigma-aldrich
2. Methyl methacrylate (MMA)	purity, 99%	Sigma-aldrich
3. Octadecane (OD)	purity, 99%	Aldrich
4. Benzoyl peroxide (BPO)	72-77%	Sigma-aldrich
5. Polyoxyethylene sorbitan monooleate (Tween80)	purity, 90%	Sigma-aldrich
6. Poly (vinyl alcohol) (PVA)	Hydrolyzed, 87-90%	Sigma-aldrich
7. Sodium dodecyl sulfate (SDS)	Analytical reagent	Sigma-aldrich
8. Sodium hydroxide (NaOH)	99%	Univar
9. Sodium nitrite ($NaNO_2$)	Analytical reagent	Univar
10. Aluminum oxide (Al_2O_3)	Chromatographic	Fluka

Name	Grade	Brand
11. Calcium chloride ($CaCl_2$)	Analytical reagent	Univar
12. 2-Propanol	Analytical reagent	RCI Labscan
13. Nitrogen gas (N_2)	99.99%	Praxair

3.1.2 Instruments

Name	Model	Brand
1. Optical microscope (OM)	SK-100 EB	Seek
2. Dynamic light scattering (DLS)	Delsa^{TM} Nano C	Beckman Coulter
3. Differential scanning calorimeter (DSC)	DSC 4000	Perkin Elmer
4. Thermogravimetric analyzer (TGA)	TGA 4000	Perkin Elmer
5. Scanning electron microscope (SEM)	JSM 5610	Jeol
6. Hot air oven	UNB 400	Memmert
7. Vacuum oven	D2F-6051	-
8. Mechanical stirrer	RW	IKA

3.2 Experiments

3.2.1 Preparation of PDVB/OD microcapsules by microsuspension polymerization

The PDVB/OD microcapsules were prepared by two steps. Firstly, oil droplets were prepared by PIE at 4 mL/min of aqueous phase additional rate. They were then subsequently polymerized to prepare polymer microcapsules. The PDVB/OD microcapsules were prepared by microsuspension polymerization of the oil droplets prepared by the PIE compared with conventional technique under the conditions listed in Table 3.1

Table 3.1 Reagent amounts and procedure for the preparation of PDVB/OD microcapsules by microsuspension polymerization[a] of DVB/OD droplets prepared by mechanical stirring [b]

Phase	Ingredients	Experiment[c]									
		1	2	3	4	5	6	7	8	9	10
Oil	DVB (g)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	OD (g)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	BPO (g)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	Tween80(g)	10.0	10.0	10.0	-	-	-	-	-	-	-
	PVA (g)	-	-	-	1.0	2.0	2.0	3.0	3.0	3.0	3.0
Aque-	SDS (g)	-	-	-	-	-	-	-	-	0.1	0.1
ous	$NaNO_2$ (g)	-	0.02	0.04	-	-	0.02	-	0.02	-	-
	Water (g)	79.6	79.5	79.5	89.6	87.6	87.5	86.6	86.5	86.5	86.5

[a] 80 ˚C, 24 hours, stirring rate at 200 rpm and 10 min purging with N_2

[b] 500 rpm, 20 min

[c] Experiments 1-9 used the PIE method while experiment 10 employed the conventional method for oil droplets preparation

3.2.1.1 Preparation of DVB/OD droplets by PIE method

The DVB/OD oil droplets were prepared by PIE as the procedure shown in Fig. 3.1. The oil and aqueous phases were separately prepared as follows. Firstly, 1:1 ratio of DVB and OD were homogeneously mixed with BPO (8% wt of monomer) and various kinds of surfactants (3-10% wt of total solution) as oil phase. Consequently, the aqueous phase with and without SDS (0.1% wt of total solution) and $NaNO_2$ were gradually dropped into the oil phase at an additional rate of 4 mL/min under mechanical stirring at 500 rpm. The water in oil (W/O) system was firstly formed by the adsorption of surfactant at the droplet interface. When the amounts of aqueous medium increased until higher than the amount of oil phase, then, oil in water (O/W) emulsion was formed called phase inversion.

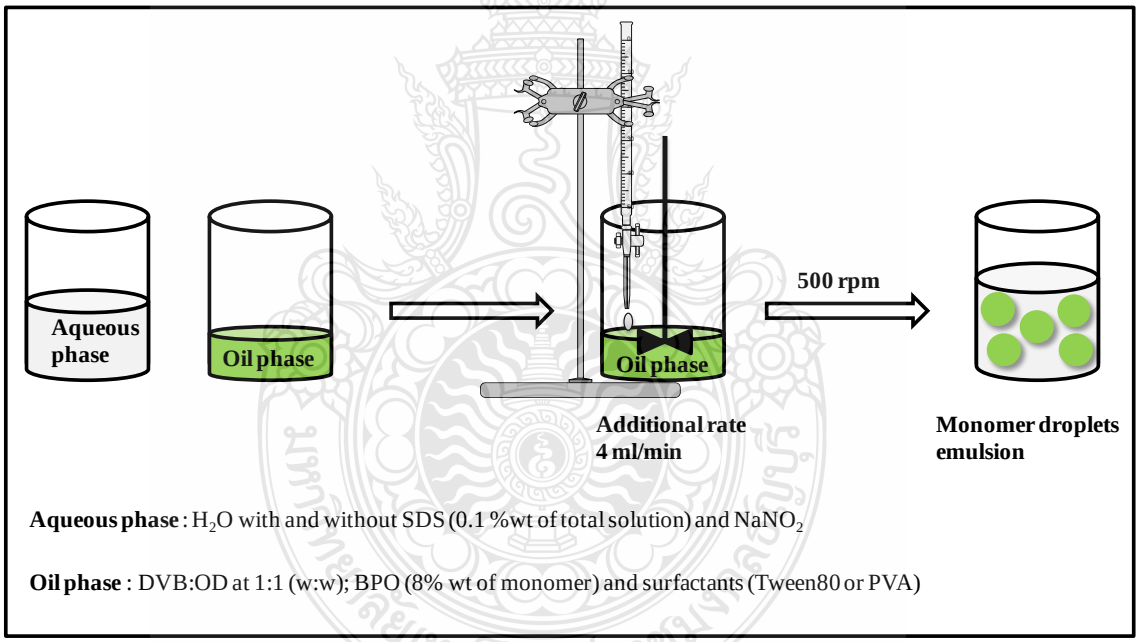


Figure 3.1 Schematic of the preparation process of DVB/OD droplets by PIE

3.2.1.2 Preparation of DVB/OD droplets by conventional emulsification method

DVB/OD droplets were also prepared by the conventional emulsification method using mechanical shear rate. The oil phase was prepared by mixing of 1:1 ratio of DVB:OD and BPO (8 wt % of monomer). It was poured into the PVA aqueous solution containing SDS (0.1% wt of total solution) and then homogenized at 500 rpm for 10 min to form DVB/OD droplets as shown in Fig. 3.2.

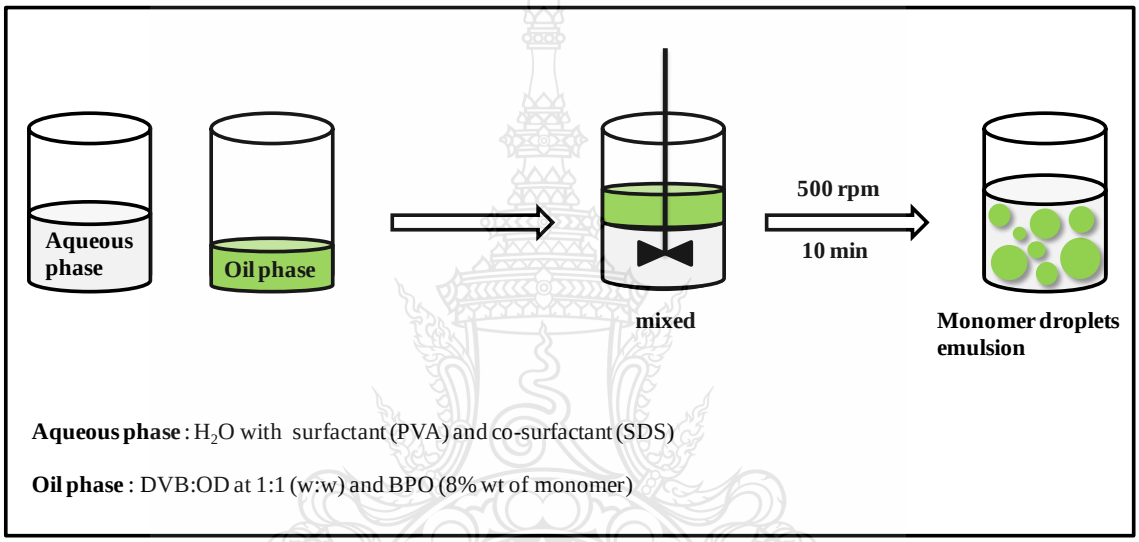


Figure 3.2 Schematic of the preparation process of the DVB/OD droplets by conventional emulsification method

3.2.1.3 Preparation of PDVB/OD microcapsules by microsuspension polymerization

The obtained monomer droplet suspensions of both techniques were separately transferred to a round-bottom schlenk flask. The flask was then closed off with silicone rubber septum and degassed using several N_2/vacuum cycles. It was put into an oil bath at 80 ^{o}C and polymerized for 24 hour with magnetic stirring rate of 500 rpm. The schematic of the preparation of the PDVB/OD microcapsules by microsuspension polymerization was shown in Fig. 3.3

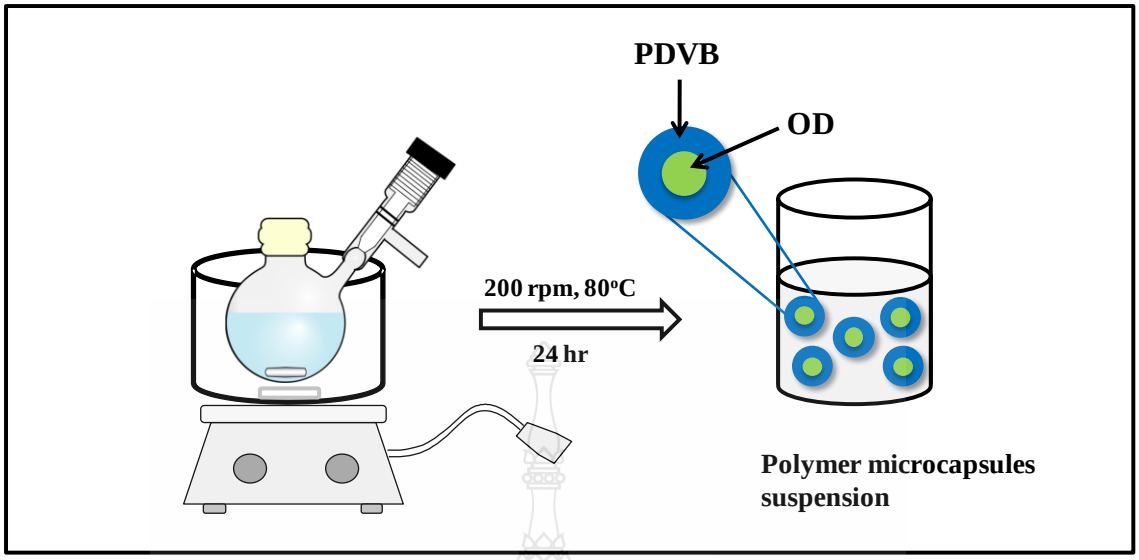


Figure 3.3 Schematic of the preparation process of the PDVB/OD microcapsules by microsuspension polymerization

3.2.2 Washing process of PDVB/OD microcapsules

After synthesis, the obtained suspension was transferred to separating funnel and left overnight. The two separated layers of the suspension were observed. The aqueous medium at the bottom layer was carefully removed. The top microcapsule layer was filtered and washed with 2-propanol before dry overnight in a vacuum oven at room temperature. The schematic of the washing process of the PDVB/OD microcapsule was shown in Fig. 3.4. The optimum washing time was studied.

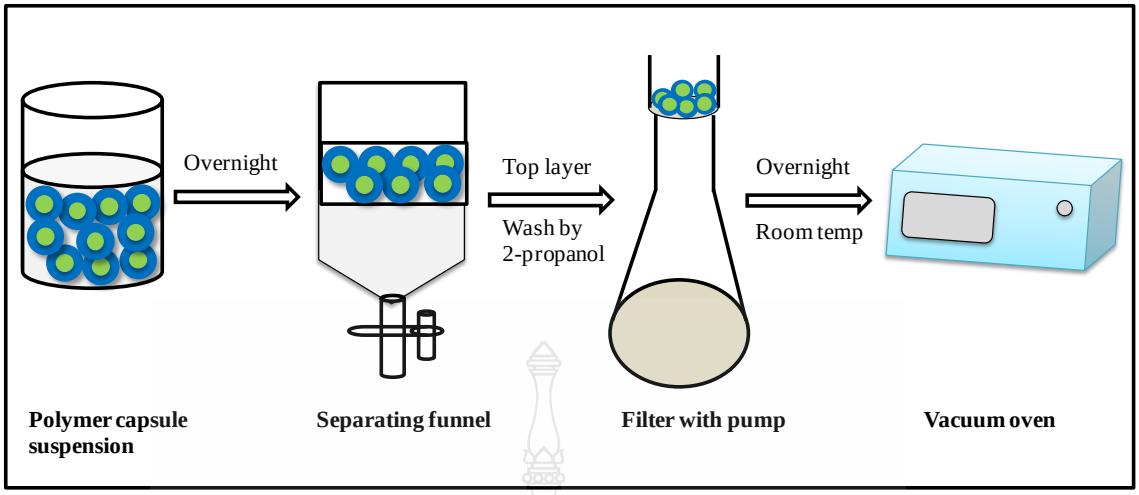


Figure 3.4 Schematic of the washing process of PDVB/OD microcapsules

3.2.3 Preparation of P(DVB-MMA)/OD microcapsules by microsuspension polymerization

3.2.3.1 Preparation of (DVB-MMA)/OD droplets by PIE

The (DVB-MMA)/OD droplets were prepared by PIE as the procedure shown in Fig. 3.1. Firstly, the oil phase of DVB and MMA (50:50 and 30:70 wt %) were mixed with OD, BPO (8 wt % of monomer) and PVA (1-3 wt % of total solution). Consequently, the aqueous phase with and without SDS (0.1 wt % of total solution) was gradually dropped into the oil phase at various additional rates under mechanical stirring at 500 rpm. A homogeneous solution of oil phase droplets dispersed in the aqueous phase was formed. The influence of the aqueous phase additional rate and surfactant concentration on the formation of oil droplets were studied.

1) Study of the aqueous phase additional rate

(DVB-MMA)/OD droplets using DVB:MMA at 50:50 (wt %) were prepared by PIE at 2, 4 and 8 mL/min of aqueous phase additional rate using the condition listed in Table 3.2. They were then subsequently polymerized to prepare polymer microcapsules.

Table 3.2 Reagent amounts and procedure for the preparation of P(DVB-MMA)/OD microcapsules by microsuspension polymerization[a] of (DVB-MMA)/OD droplets prepared by PIE[b] with various aqueous phase additional rates

Phase	Ingredients	DVB:MMA (wt %)	
		50:50[c]	30:70
Oil	DVB (g)	2.5	1.5
	MMA (g)	2.5	3.5
	OD (g)	5.0	5.0
	BPO (g)	0.4	0.4
	PVA (g)	3.0	3.0
Aqueous	SDS (g)	0.1	0.1
	Water (g)	86.5	86.5

[a] 80 ˚C, 24 hours, stirring rate at 500 rpm

[b] 500 rpm

[c] 2, 4 and 8 mL/min of aqueous phase additional rate

2) Study of the surfactant concentration

The influence of surfactants; PVA and SDS, concentration on the colloidal stability of the prepared microcapsules was investigated. The (DVB-MMA)/OD droplets were prepared by PIE of aqueous phase additional rate 2 mL/min. The oil phase with various PVA and SDS concentrations using the conditions listed in Table 3.3

Table 3.3 Reagent amounts and procedure for the preparation of P(DVB-MMA)/OD microcapsules by microsuspension polymerization[a] of (DVB-MMA)/OD droplets prepared by PIE[b] using various kinds of surfactant

Phase	Ingredients	PVA (SDS) concentration (wt %)				
		1 (0)	3 (0)	0 (0.1)	1 (0.1)	3 (0.1)
Oil	DVB (g)	2.5	2.5	2.5	2.5	2.5
	MMA (g)	2.5	2.5	2.5	2.5	2.5
	OD (g)	5.0	5.0	5.0	5.0	5.0
	BPO (g)	0.4	0.4	0.4	0.4	0.4
	PVA (g)	1.0	3.0	-	1.0	3.0
Aqueous	SDS (g)	-	-	0.1	0.1	0.1
	Water (g)	88.6	86.6	89.5	88.5	86.5

[a] 80°C, 24 hours, stirring rate at 500 rpm

[b] 2 mL/min of aqueous phase additional rate, 500 rpm

The optimum condition for the preparation of (DVB-MMA)/OD droplets using DVB:MMA at 50:50 (wt %) was used for the preparation of DVB:MMA of 70:30 (wt %) droplet.

3.2.3.2 Preparation of (DVB-MMA)/OD droplets by conventional emulsification method

(DVB-MMA)/OD droplets were also prepared by conventional emulsification technique under the conditions listed in Table 3.4. The homogeneous oil phase of DVB:MMA (wt %) of 50:50, OD and BPO (8 wt % of monomer) was firstly prepared. It was added to the aqueous phase containing PVA and SDS. The emulsification was carried out by mechanical stir at 1,500 rpm for 10 min resulting in the formation of oil phase droplets dispersed in the aqueous phase. The reagent amounts and produce for the preparation of P(DVB-MMA)/OD microcapsules by the conventional emulsification method was shown in Table 3.4.

Table 3.4 Reagent amounts and procedure for the preparation of P(DVB-MMA)/OD mirocapsules by microsuspension polymerization [a] of (DVB-MMA)/OD droplets prepared by conventional method of DVB:MMA (wt %): 50:50 with mechanical stir [b] using various amounts of PVA

Phase	Ingredients	PVA (wt %)	
		1	3
Oil	DVB (g)	2.5	1.5
	MMA (g)	2.5	3.5
	OD (g)	5.0	5.0
	BPO (g)	0.4	0.4
Aqueous	PVA (g)	1.0	3.0
	SDS (g)	0.1	0.1
	Water (g)	88.5	86.5

[a] 80 ℃, 24 hours, stirring rate at 500 rpm

[b] 1,500 rpm

3.2.3.3 Preparation of P(DVB-MMA)/OD microcapsules by microsuspension polymerization

The monomer droplet suspensions prepared by both PIE and conventional emulsification methods were separately transferred to a round-bottom schlenk flask. The procedure is the same as the PDVB/OD microcapsule preparation. The schematic of the preparation of the P(DVB-MMA)/OD microcapsules by microsuspension polymerization was shown in Fig. 3.5

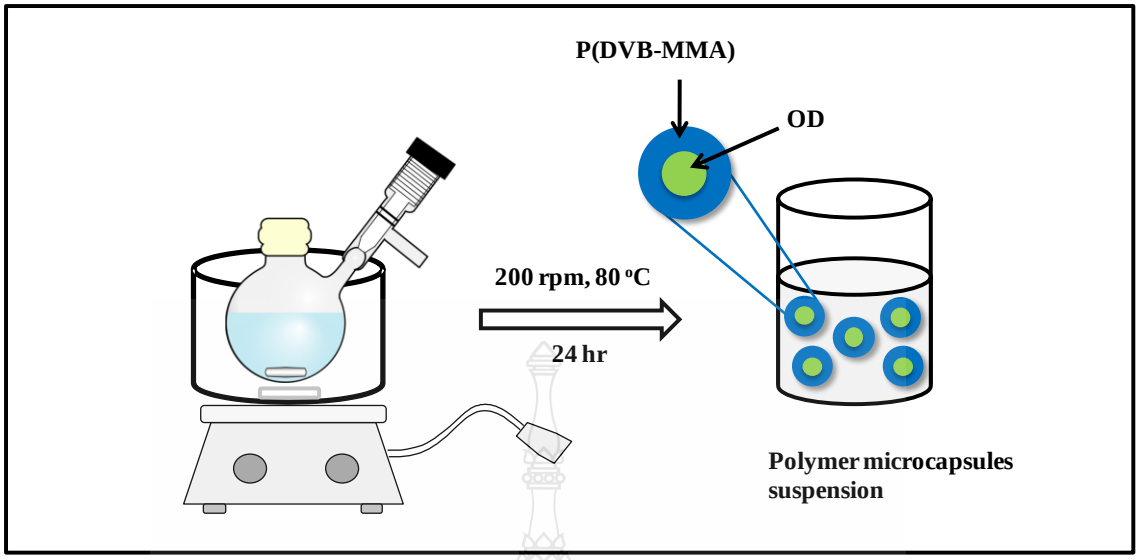


Figure 3.5 Schematic of the preparation process of P(DVB-MMA)/OD microcapsules by microsuspension polymerization

3.2.4 The study of the partitioning of PVA in oil/aqueous phase

The oil phase containing DVB, MMA, OD and PVA was firstly prepared under the conditions listed in Table 3.5. After that, the aqueous phase was slowly dropped at 2 mL/min with gentle stirring rate. The mixture of oil and aqueous phase was transferred to a round bottom flask. It was put in an oil bath at 80 ^{o}C for 2 hours with a mild stirring rate. After the stirring was stopped, the mixture was kept until the phase separation as clearly observed. Then, the aqueous phase was taken out. The amount (wt %) of PVA existed in an aqueous phase was then measured by gravimetry whereas that value in the oil phase was obtained from the subtraction of PVA in an aqueous phase from the total PVA.

Table 3.5 Reagent amounts and procedure for the study of partitioning of PVA using the polymerization condition [a]

Phase	Ingredients	PVA (wt %)	
		1	3
Oil	DVB (g)	2.5	2.5
	MMA (g)	2.5	2.5
	OD (g)	5.0	5.0
	PVA (g)	1.0	3.0
Aqueous	Water (g)	89.0	87.0

[a] 80 ˚C, 2 hours, stirring rate at 200 rpm

3.3 Characterization of PDVB/OD and P(DVB-MMA)/OD microcapsules

The properties of the prepared PDVB/OD and P(DVB-MMA)/OD microcapsules were characterized as follows. Weight- and number- average particle diameters (d_w and d_n, respectively) were measured by dynamic light scattering (DLS) (Delsa Nano-C, Beckman Coulter, USA) with a light scattering angle of 165^o at room temperature. Polymer suspension samples (approximately 10 wt %) withdrawn from the reactor were directly measured using the concentration mode of DLS. The prepared microcapsules were observed with an optical microscope (OM) (SK-100EB & SK-100ET, Seek, Seek Inter Co. Ltd., Thailand) and scanning electron microscope (SEM) (JSM-6510, JEOL, JEOL Ltd., Japan) to investigate the inner structure of the microcapsules and the morphology of the surface, respectively. For SEM observation, one drop of the microcapsule suspension was placed on a nickel SEM stub and dried before coated with Au. The thermal properties of the microcapsules were determined by a thermogravimetric analyzer (TGA) (TGA 4000, Perkin-Elmer, USA) and a differential scanning calorimeter (DSC) (DSC 4000, Perkin-Elmer, USA). The degradation temperatures of pure OD and the microcapsule were measured with TGA using a heating rate of 5 ^{o}C/min. The latent heats of crystallization (H_c) and melting (H_m) and the crystallization (T_c) and melting (T_m) temperatures of the encapsulated OD in a dry

state were measured with a DSC under N_2 flow with a scanning temperature range and rate of -20-40 ^{o}C and 5 ^{o}C/min, respectively. To compare the H_c and H_m values of the encapsulated OD in the microcapsules having different amounts OD, the H_c and H_m values were expressed in a unit of joules per 1 g of encapsulated OD (J/g-OD). These values were calculated from the cooling/heating peak area of the DSC thermogram, and the OD content obtained from the TGA analysis using the following equation.

$$A = (B/C) \times 100 \text{ ----------} 3.1$$

Where

A = H_m and H_c of the encapsulated OD in unit of joules per 1 g of the encapsulated OD (J/g-OD)

B = H_m and H_c of the encapsulated OD in the dried microcapsules obtained from the DSC thermogram (J/g-sample)

C = % OD in the dried microcapsules obtained from the TGA thermogram

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Preparation of PDVB/OD microcapsules by microsuspension polymerization

4.1.1 Influence of surfactant types and amounts

The utilization of high shear rate to produce the oil droplets and a broad particle size distribution of the obtained microcapsules are two main disadvantages of microencapsulated heat storage materials prepared by microsuspension polymerization. Therefore, in this work, PIE is chosen to replace of the conventional one for the preparation of the oil droplets used in the microsuspension polymerization. The droplets were formed without a high shear rate by the dropwise addition of a larger amount of water, with and without SDS as a cosurfactant in a smaller amount of the oil phase containing surfactant. The surfactant gradually moved to the oil-water interface stabilizing the oil droplets during water addition. The influence of surfactant types (Tween 80 and PVA) dissolved in the oil phase on the colloidal stability of the microcapsules was studied.

Table 4.1 Weight- and number average diameters and particle size distribution [a] of PDVB/OD microcapsules prepared by microsuspension polymerization with Tween80 as surfactant at various $NaNO_2$ concentrations using PIE for oil droplets generation

$NaNO_2$ (wt %)[b]	Conversion (%)	d_w (nm)	d_n (nm)	d_w/d_n
0.0	57	660	456	1.45
0.02	19	28,276	65	436.36
0.04	23	568	34	16.55

[a] Measured with DLS

[b] Related to the procedure and reagent in Table 3.1

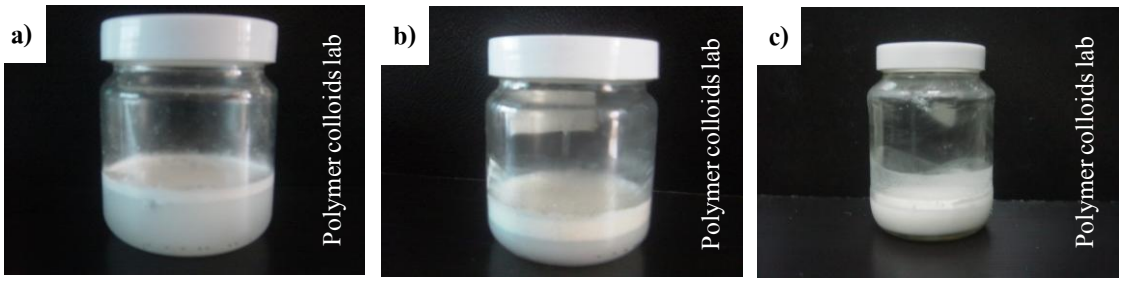


Figure 4.1 The suspension photos of PDVB/OD microcapsules prepared by microsuspen- sion polymerization: oil droplets generated by PIE, using Tween 80 in oil phase at various $NaNO_2$ concentrations in an aqueous medium (wt %): a) 0; b) 0.02 and c) 0.04

In the case of Tween 80, when using a concentration lower than 10 wt % (related to total solution), the polymer microcapsule was unable to prepare and large coagulation was observed during the polymerization. At 10 wt % of Tween 80, microcapsules with a nanometer size diameter (d_w = 660 and d_n = 456 nm) and a quite narrow PSD (d_w/d_n = 1.45) were formed as shown in Table 4.1. Moreover, the colloidal stability was quite improved because of the decreased of coalescence of the obtained capsules. However, some of the homopolymer of PDVB particles seemed to be produced as shown in Fig. 4.1a, where turbid dispersion was observed in the bottom part of the suspension. Microencapsulated PDVB/OD floated on the top of the suspension because of its low total density (OD = 0.8 g/ml, PDVB = 1.04 g/ml [8] and PDVB/OD = 0.9 g/ml related to the recipe; 1:1 of DVB:OD) compared with water. Therefore, the particles dispersed in the bottom part were PDVB which may be polymerized in the micelle formed by Tween80 via emulsion polymerization giving polymer particle of nanometer size. During the polymerization, some of Tween80 that firstly dissolved in the monomer phase may then diffuse to the continuous phase during the addition of water. Thus, the micelle was formed and played a role as polymerization loci competing with the monomer droplets. Because OD is much more hydrophobic than DVB, it is unable to diffuse via water (the continuous phase) to the micelle as the monomer is. As a result, only the PDVB particles polymerized in the micelle were dispersed in the bottom part of the suspension.

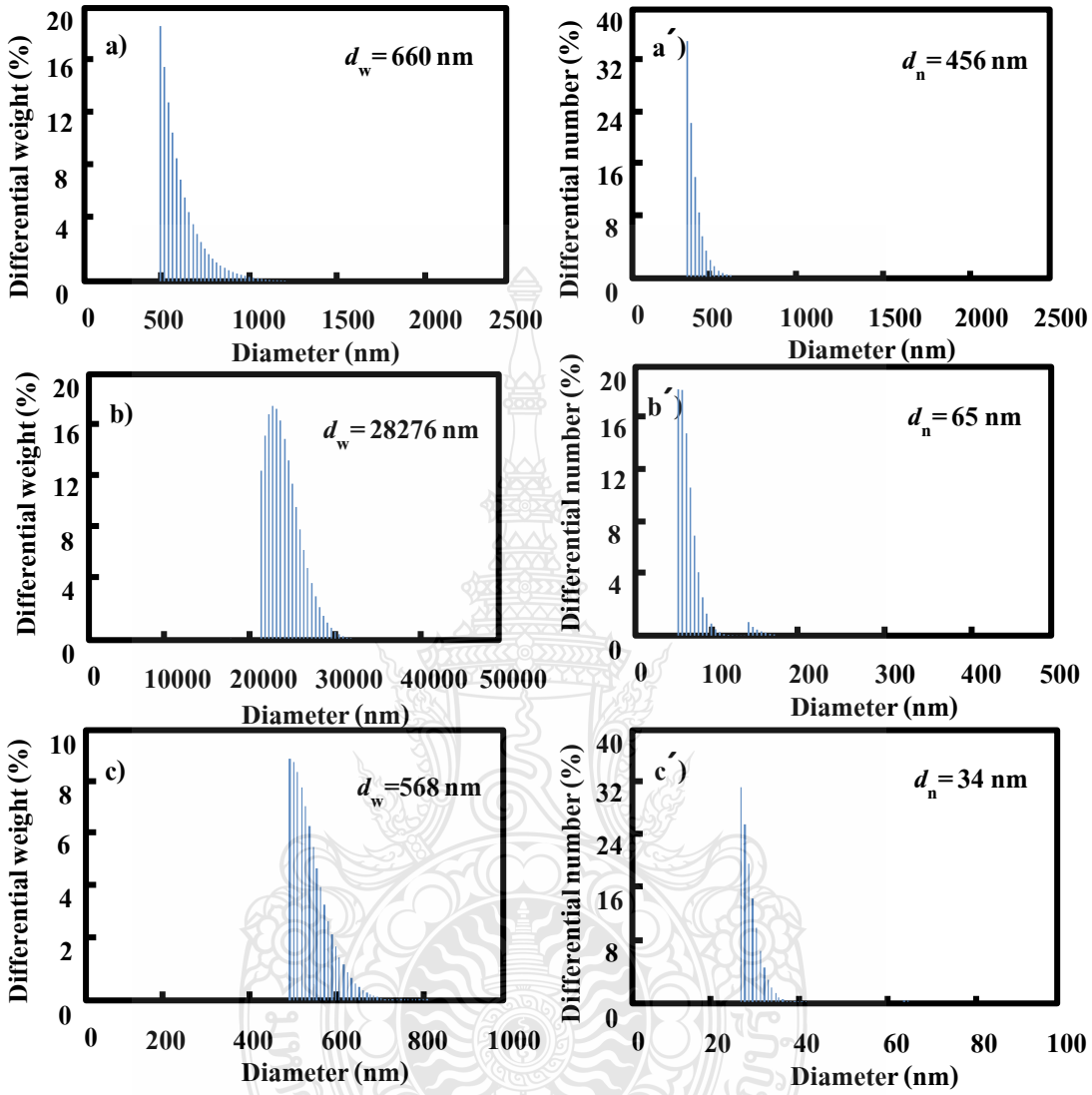


Figure 4.2 Weight- (d_w) and number (d_n) average diameters of PDVB microcapsules prepared by microsuspension polymerization: oil droplets generated by PIE, using Tween80 in oil phase at various $NaNO_2$ concentrations in an aqueous medium (wt %): (a, a') 0; (b, b') 0.02 and (c, c') 0.04

To depress emulsion polymerization in an aqueous medium, the water soluble inhibitor as $NaNO_2$ was added to the system as represent in the experiment 2 (0.02 % related to total reagent) and 3 (0.04 % related to total reagent). The radical or oligomeric radical exiting from the monomer droplets would scavenger with $NaNO_2$ in the aqueous medium which may reduce the emulsion polymerization.

However, the data in Table 4.1, Fig. 4.1 and 4.2 represented that the secondary nucleation was not significantly decreased. The aqueous medium of both conditions were still turbid as shown in Fig. 4.1b and c. It is accord with DLS data that the small particles were still observed as shown in Fig. 4.2a and b. In addition, the percent conversions (19 and 23% for 0.02 and 0.04 wt % of $NaNO_2$, respectively) were quite decreased from that of the polymerization without $NaNO_2$ (57%). It can be explained that in the case of without $NaNO_2$, polymerization would predominantly took place in the aqueous medium as emulsion polymerization. Because much more amount (10 wt %) of Tween80 than its CMC (0.16 wt %) was used, a large number of micelles existed in aqueous medium. Then, the highest conversion was obtained. The percent conversion decreased with the increase of the inhibitor ($NaNO_2$) concentration in aqueous medium. Therefore, it seems that using Tween 80 is inappropriate for producing PDVB/OD microcapsules in microsuspension polymerization because of the formation of unencapsulated OD particle byproduct and the utilization of large amounts of surfactant.

Generally, PVA prefer to use as stabilizer of suspension polymerization. Therefore, it then was selected instead of Tween80. Various amounts (1-3 wt % related to total reagent) of PVA with/without $NaNO_2$ were added into the oil phase as Experiment 4-8. Low amounts of PVA (1.0 and 2.0 wt %) were completely dissolved in the oil phase whereas it was quite difficult to dissolve completely in the case of 3 wt %. However, the solution was homogeneous without precipitation of PVA after shaking for several minutes.

Table 4.2 Weight- and number average diameters and particle size distribution [a] of PDVB/OD microcapsules prepared by microsuspension polymerization with various PVA concentrations ($NaNO_2$ concentration) using PIE for oil droplets generation

PVA ($NaNO_2$) (wt %)[b]	Conversion (%)	d_w (nm)	d_n (nm)	d_w/d_n
1 (0)	-	375	259	1.45
2 (0)	-	41,333	2,066	20.00
2 (0.02)	10	11,082	1,096	10.10
3 (0)	-	30,155	1,315	22.93
3 (0.02)	18	6,052	1,272	4.76

[a] Measured with DLS

[b] Related to the procedure and reagent in Table 3.2

The coagulation was observed in all conditions including the addition of $NaNO_2$ although it gradually decreased with the increase of PVA content (Fig. 4.3). Because of the coagulation, it was difficult to obtain the percent conversion and PSD as shown in Table 4.2 and Fig. 4.4, respectively. In addition, the obtained d_w and d_n were not reliable effecting from the particle coagulation as well. In the case of 1.0 wt % of PVA, microcapsules with a nanometer size diameter (d_w = 374 and d_n = 259 nm) and a quite narrow PSD (d_w/d_n = 1.45) was formed according with PSD obtained by DLS of Fig. 4.4 (a, a'). The data seem good.

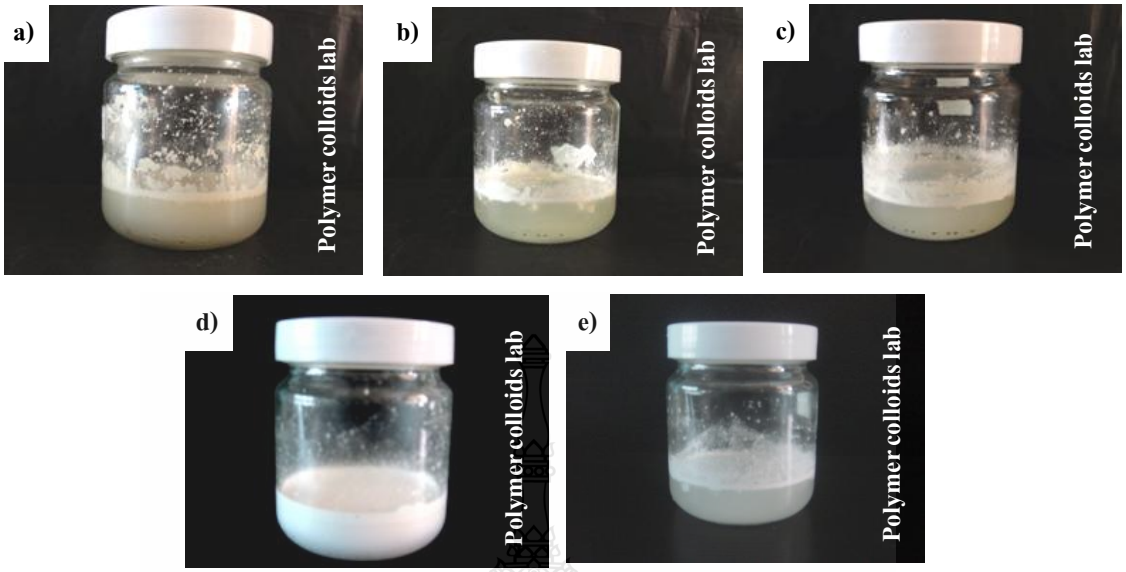


Figure 4.3 The suspension photos of PDVB/OD microcapsules prepared by microsuspen- sion polymerization: oil droplets generated by PIE, using various amounts of PVA in oil phase and various $NaNO_2$ concentrations in aqueous medium (wt %): a) 1 (0); b) 2 (0); c) 2 (0.02); d) 3 (0) and e) 3 (0.02)

However, the dispersion sample which was sampling from the reactor for DLS measurement contained only a few amounts of capsule particles due to most of them representing coagulation. Therefore, it was so difficult to obtain the main particles size. Similar phenomena were obtained with the increase in PVA amount. It seems that the microcapsules were not successfully prepared using only PVA even though at high concentration (3 wt %). However, it is quite difficult to further increase the PVA concentration because of its low solubility in the oil phase.

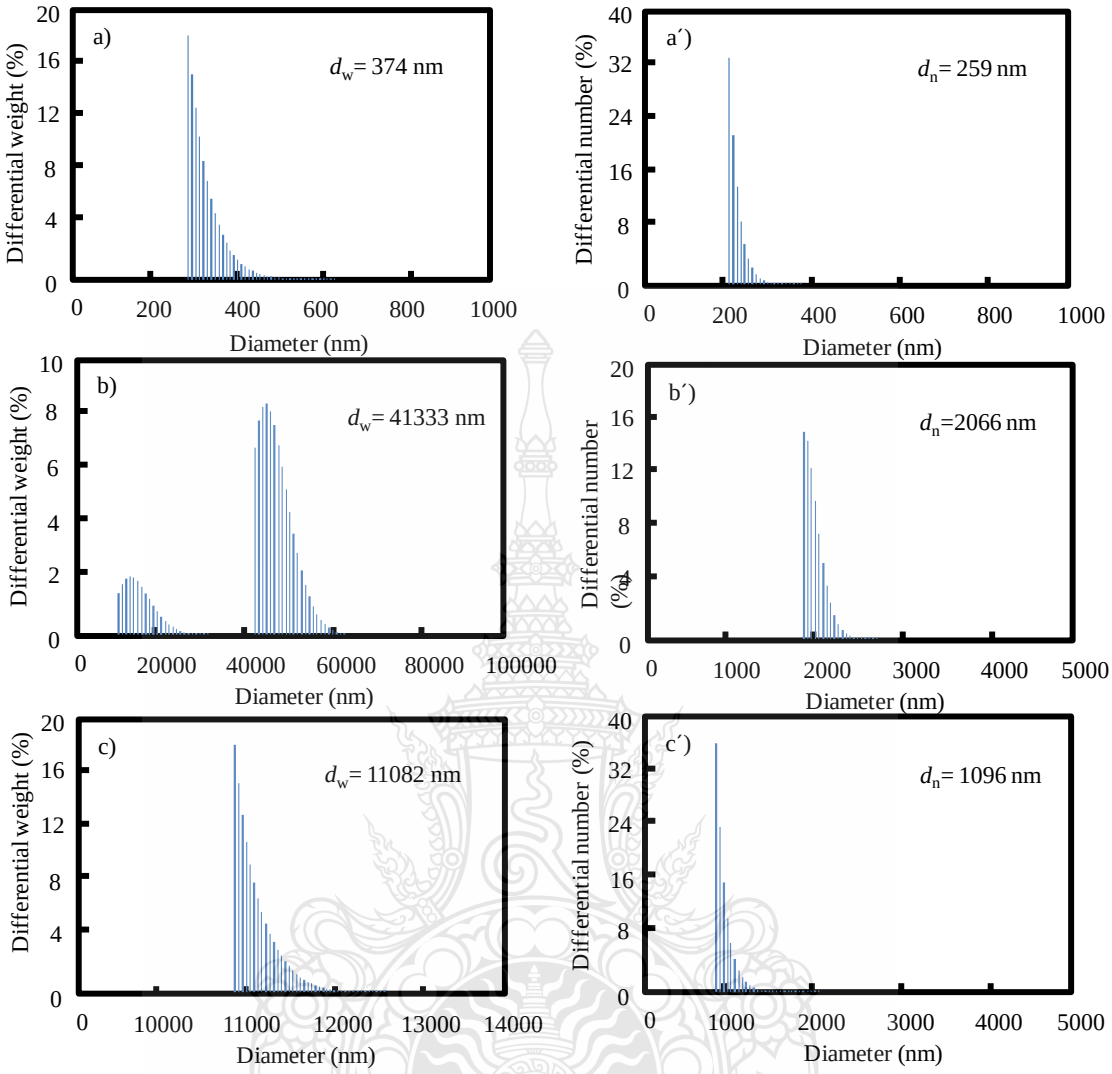


Figure 4.4 Weight- and number average diameters (d_w and d_n), respectively, of PDVB/ OD microcapsules prapared by microsuspension polymerization: oil droplets generated by PIE, using various amounts of PVA in oil phase ($NaNO_2$ concentration in an aqueous medium) (% wt): (a, a´) 1(0); (b, b´) 2(0); (c, c´) 2(0.02); (d, d´) 3(0) and (e, e´) 3(0.02)

(Fig. 4.4 continued)

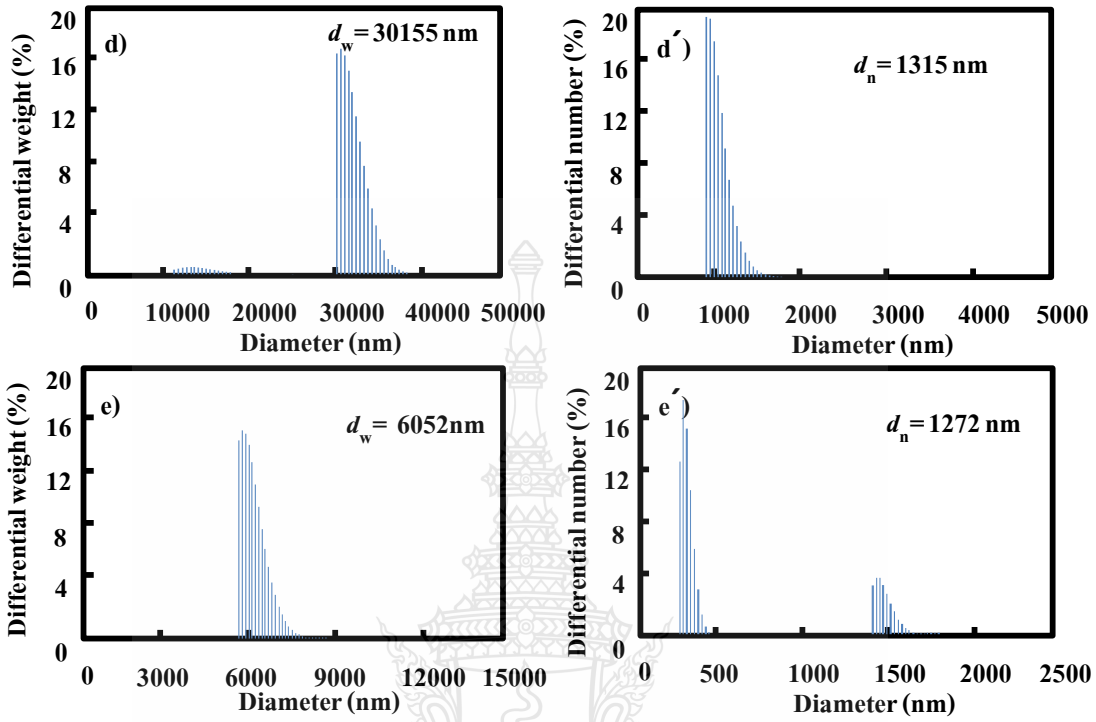


Figure 4.4 Weight- and number average diameters (d_w and d_n), respectively, of PDVB/ OD microcapsules prapared by microsuspension polymerization: oil droplets generated by PIE, using various amounts of PVA in oil phase ($NaNO_2$ concentration in an aqueous medium) (% wt): (a, a´) 1(0); (b, b´) 2(0); (c, c´) 2(0.02); (d, d´) 3(0) and (e, e´) 3(0.02)

To overcome this problem, small amounts (0.1 wt % related to total solution) of the anionic surfactant as SDS were added into the aqueous medium before PIE process. Micelles of SDS were not formed because the amount added was lower than it CMC (CMC, approximately 0.2 wt %) [56]. Therefore, SDS might predominantly adsorb at the monomer droplet surface, performing as a cosurfactant. The dispersion state was shown in Fig. 4.5a, where most of the particles floated on the top of the emulsion. The particle coagulation was not observed. Therefore, the microcapsules of PDVB/OD were success- fully prepared in the presence of PVA (3 wt %) and SDS (0.1 wt %) in oil phase and aqueous medium, respectively. The obtained

PDVB/OD microcapsules, approximately 2 μm size (d_w = 1.55 and d_n = 1.49 μm) and a narrow PSD (d_w/d_n = 1.04) were observed as shown in Table 4.3. These results accorded with the PSD as shown in Fig. 4.6 (a, a´). This indicates that droplet nucleation predominantly took place in this system. It can be concluded that the utilization of cosurfactant (SDS) cooperative with surfactant (3 wt % of PVA) improved the colloidal stability of PDVB/OD droplets and microcapsules.

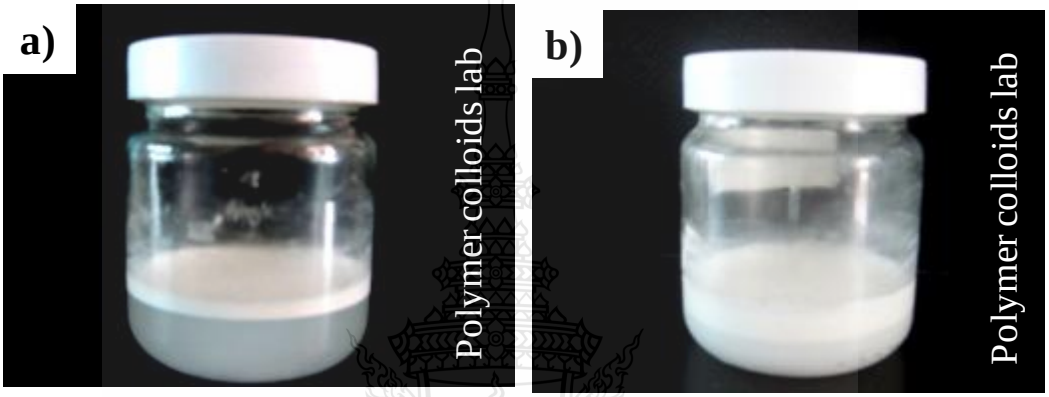


Figure 4.5 The suspension photos of PDVB/OD microcapsules prepared by microsuspen- sion polymerization using PVA (3 %wt) and SDS (0.1 %wt) as surfactant and cosurfactant, respectively: oil droplets generated by PIE (a) and conventional technique (b)

Table 4.3 Weight- and number average diameters and particle size distribution [a] of PDVB/OD microcapsules prepared by microsuspension polymerization using PVA as a surfactant cooperative with SDS as a cosurfactant: monomer droplets generated by PIE and conventional techniques

Experiment[b]	Conversion (%)	d_w (nm)	d_n (nm)	d_w/d_n
PIE	92	1,550	1,493	1.04
Conventional	-	2,324	195	11.92

[a] Measured with DLS

[b] Related to the procedures and reagents in PIE and conventional are respectively experiment 9 and 10 (Table 3.1)

On the other hand, the microsuspension polymerization using conventional technique for monomer droplets preparation (experiment 10 in Table 3.1) was also carried out, where the same amount of both surfactants were pre-dissolved in an aqueous medium. A large coagulation with a broad PSD (d_w/d_n = 11.92) was observed. Furthermore, the turbid dispersion due to the formation of particles in the aqueous medium was clearly observed (Fig. 4.5b). It was consistent with a bimodal distribution (Fig. 4.6b) of weight average particle diameter. This agreed well with OM and SEM photographs that the PDVB/OD microcapsules prepared by the conventional method (Fig. 4.7b and b') represented larger and broader PSD than those of the PIE method (Fig. 4.7a and a'). These results indicated that monomer droplets generated by PIE method represented better control in colloidal stability than those of the conventional method.

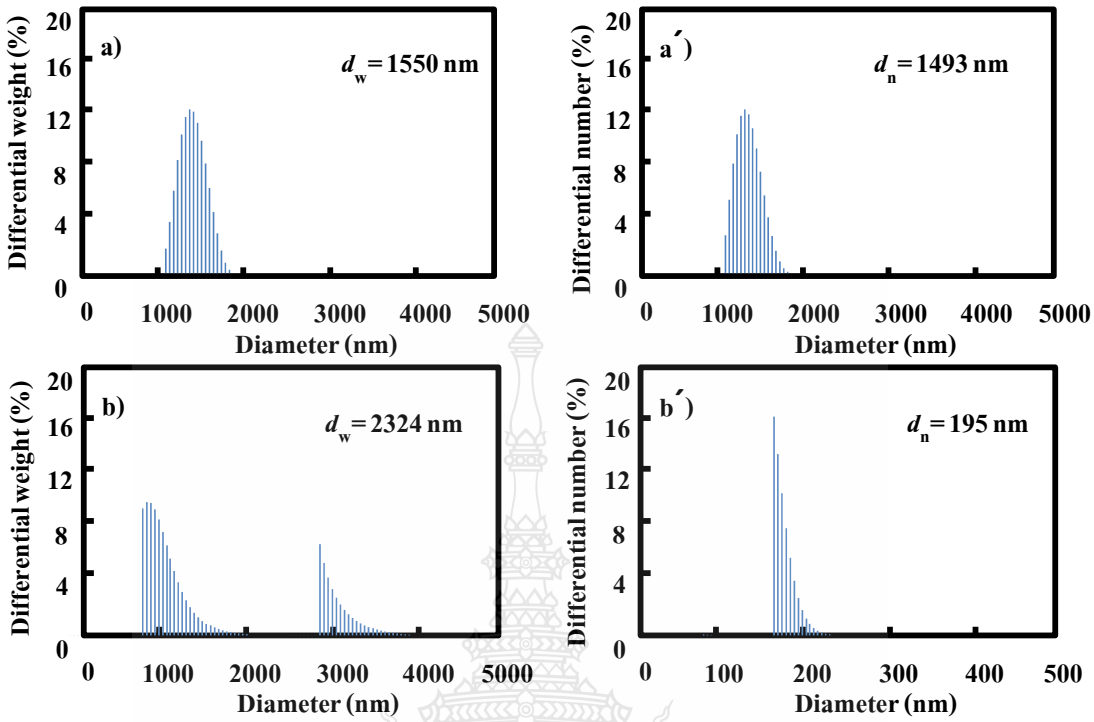


Figure 4.6 Weight- and number average diameter (d_w and d_n), respectively of PDVB/OD microcapsules prepared by microsuspension polymerization using PVA as a surfactant cooperative with SDS as a cosurfactant: monomer droplets generated by (a, a´) PIE and (b, b´) conventional techniques

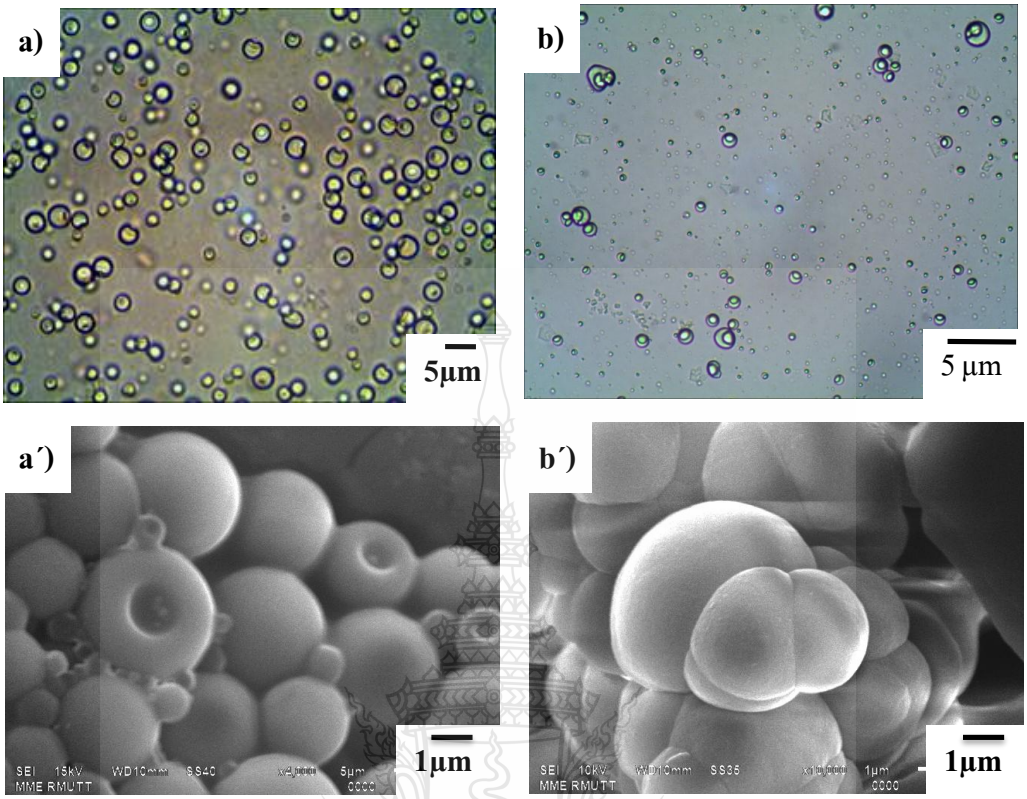


Figure 4.7 OM and SEM micrographs of PDVB/OD microcapsules prepared by microsuspension polymerization of experiments: (a, a´) PIE and (b, b´) conventional methods for monomer droplets generation

To clarify the performance of PIE method, the particle size and PSD of monomer droplets and microcapsules at before and during polymerization were studied. It was found that throughout the polymerization the particle size both d_w (1.55-1.58 µm) and d_n (1.49-1.54 µm) of microcapsules (including monomer droplet) were almost the same (Table 4.4). Moreover, the monomer droplets and polymer microcapsules have quite narrow PSDs, exhibiting d_w/d_n values in the range of 1.02-1.05 accorded with the PSD of DLS data shown in Fig. 4.8. The particle size and PSDs were maintained with the conversion as shown in Table 4.4. These results indicated that the colloidal stability of the polymer particles was well controlled throughout the polymerization without particle coagulation. According to optical (Fig. 4.9) and SEM (Fig. 4.10) micrographs, the microcapsule sizes were quite constant throughout the polymerization. The particle sizes agreed well with hydrodynamic particle diameter as

shown in Table 4.4. Moreover, the OD core was well enveloped with a PDVB shell, forming spherical PDVB/OD microcapsules with smooth outer surface and a dimple. Because the volume of the OD core gradually reduced as they went from the polymerization temperature (80 °C, lower density) to room temperature (higher density), a void was formed in each microcapsule. The dimpled capsules then would be created when the shell strength of PDVB was not enough to withstand the external pressure, similar with phenomena discussed in the previous reports [57]. However, the OD core was completely encapsulated with the PDVB shell. Therefore, the microcapsules of PDVB/OD with a narrow PSD were successfully prepared by the microsuspension polymerization of DVB/OD droplets generated by the PIE method using PVA and SDS as surfactants.

Table 4.4 Conversions, DVB/OD droplet sizes and PDVB/OD particle sizes [a] at various times during microsuspension polymerization of DVB/OD droplets produced by PIE

Time (h)	Conversion (%)	d_h (μm)	d_w (μm)	d_n (μm)	d_w/d_n
0	0	2.94	1.57	1.52	1.03
1	29	2.84	1.57	1.51	1.04
3	68	2.72	1.56	1.50	1.04
6	82	2.89	1.58	1.51	1.05
12	83	2.99	1.57	1.54	1.02
24	92	2.94	1.55	1.49	1.04

[a] Measured by DLS; D_h is hydrodynamic particle diameter

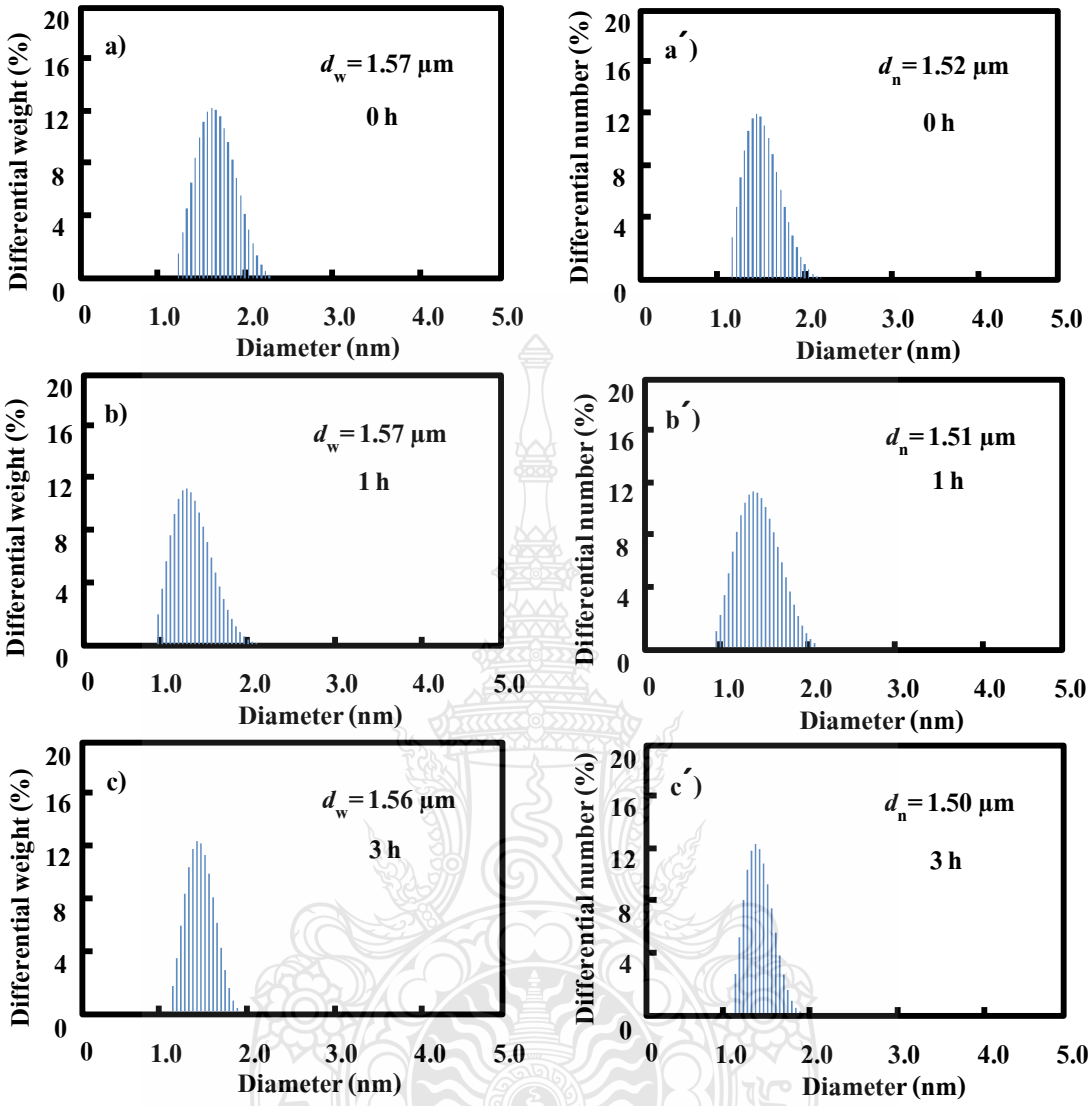


Figure 4.8 Weight- and number average diameters (d_w and d_w) respectively, of PDVB/OD microcapsules at various times during the microsuspension polymerization using PIE method for monomer droplet generation. Polymerization time (h): (a, a´) 0; (b, b´) 1; (c, c´) 3; (d, d´) 6; (e, e´) 12 and (f, f´) 24 according to Table 4.4

(Fig. 4.8 continued)

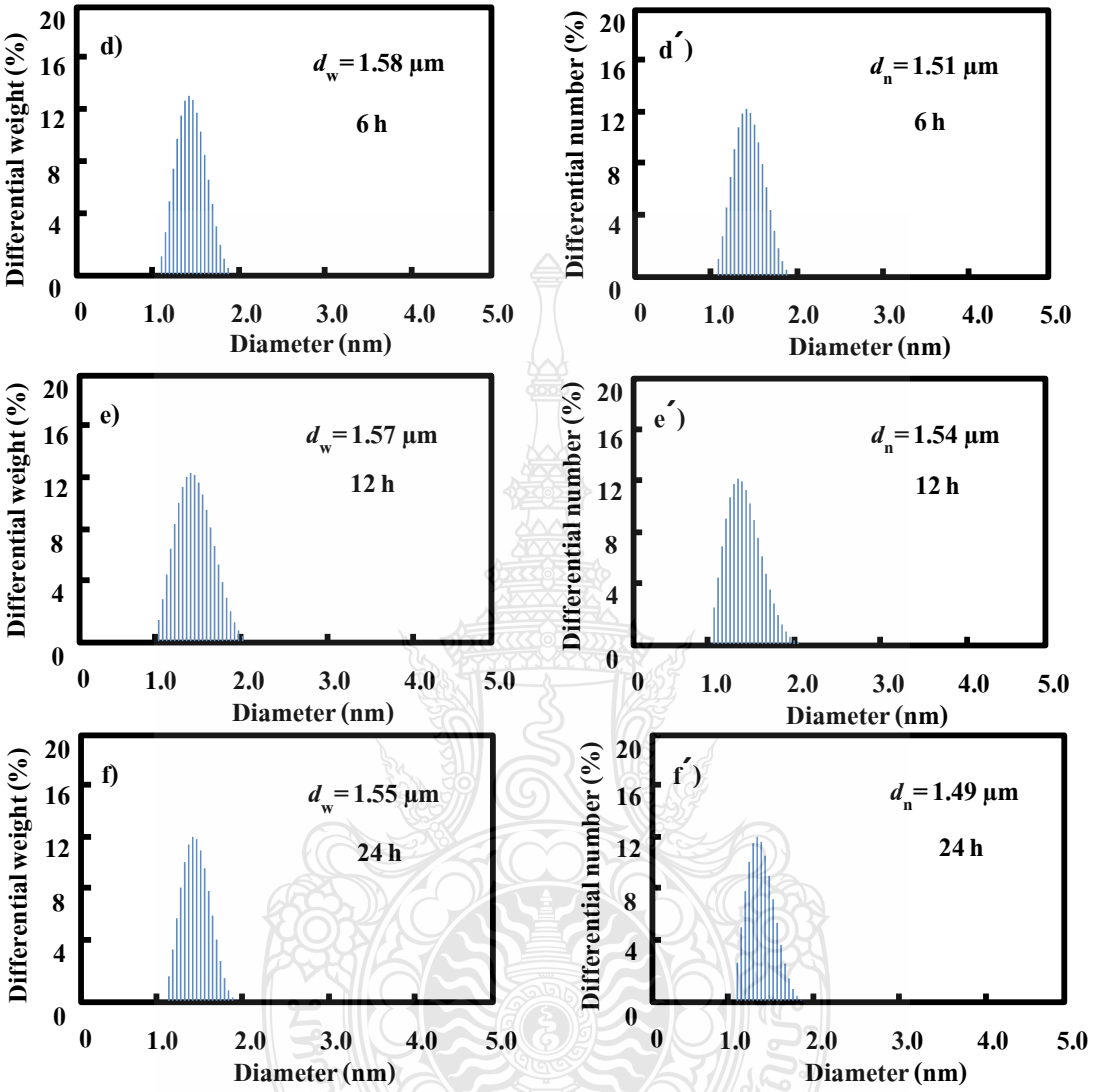


Figure 4.8 Weight- and number average diameters (d_w and d_w) respectively, of PDVB/OD microcapsules at various times during the microsuspension polymerization using PIE method for monomer droplet generation. Polymerization time (h): (a, a´) 0; (b, b´) 1; (c, c´) 3; (d, d´) 6; (e, e´) 12 and (f, f´) 24 according to Table 4.4

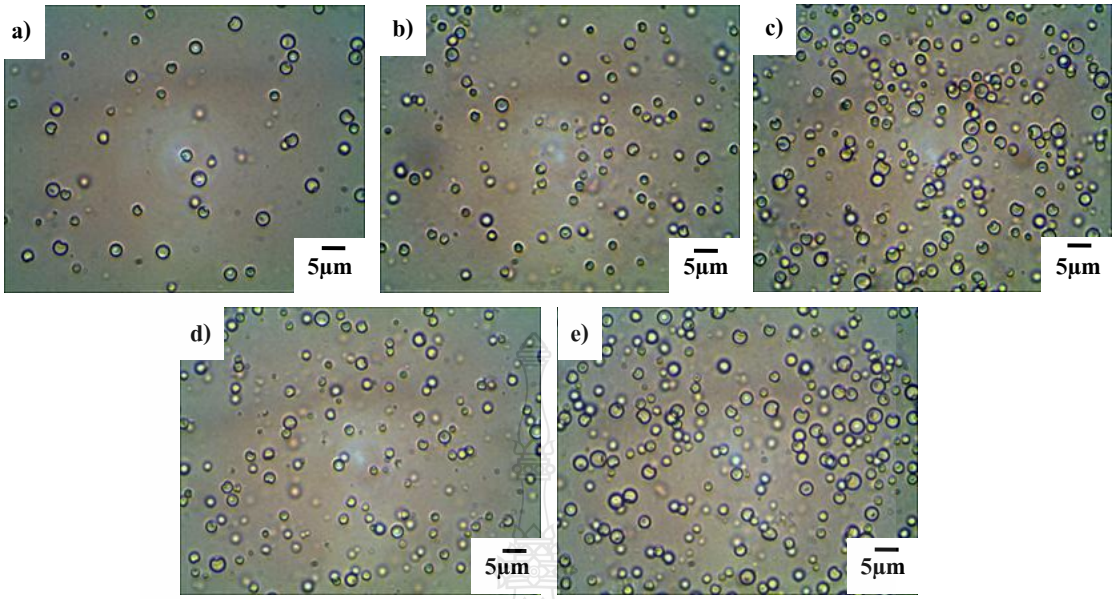


Figure 4.9 Optical micrographs of PDVB/OD microcapsules at various times during the microsuspension polymerization using PIE method for monomer droplets generation. Polymerization times (h): (a) 1; (b) 3; (c) 6; (d) 12 and (e) 24

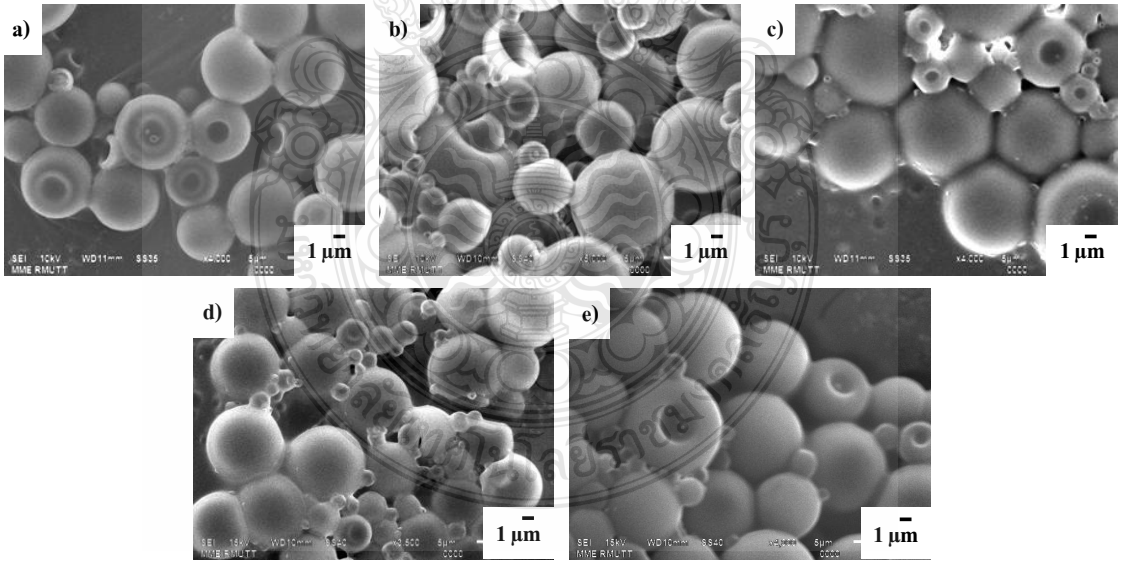


Figure 4.10 SEM micrographs of PDVB/OD microcapsules at various times during the microsuspension polymerization using PIE method for monomer droplets generation. Polymerization times (h): (a) 1; (b) 3; (c) 6; (d) 12 and e) 24

4.1.2 Washing process of PDVB/OD microcapsules

Before thermal properties measurement, the PDVB/OD microcapsules were washed with solvent to remove unencapsulated OD. Because 2-propanol is a good solvent of OD and does not dissolve PDVB, it was selected as washing solvent in this experiment. The dried microcapsules about 1 g were mixed with 5 g of 2-propanol at various times (30-120 sec). The suspensions were then filtered with PTFE membrane with a pore size of 0.45 μm. The obtained microcapsules were dried in a vacuum oven at room temperature overnight. To study the performance of washing process, the dried micro- capsules with post addition of bulk OD was also studied in the same procedure of the dried microcapsules washing process. From TGA measurement as shown in Fig. 4.11, it was found that approximately 60 % OD was remained in the microcapsules and stable throughout various washing times. Similar result was obtained in the case of the microcapsules with post addition of pure OD even though before washing the OD content was about 90 %. The OD content was about 58 % after dispersed in 2-propanol for 90 sec. These results indicated that the washing process effectively removed OD only on the particle surface. In addition, the OD seemed to be completely encapsulated by the preparation using microsuspension polymerization.

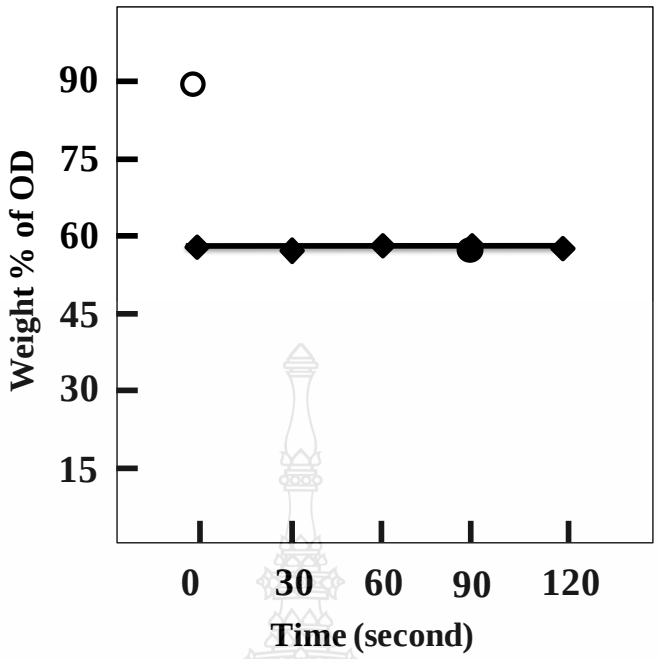


Figure 4.11 Weight % of the encapsulated OD inside PDVB/OD microcapsules prepared by microsuspension polymerization using PIE for oil droplets generation washed with 2-propanol with various times (◆) and PDVB/OD microcapsules with post addition of pure OD at before (○) and after washing (●)

4.1.3 Thermal properties of the encapsulated OD in PDVB/OD microcapsules

The thermal property in the term of latent heats (H_m and H_c) of the encapsulated OD in PDVB/OD microcapsules in a unit of joules per gram of OD (J/g-OD) was calculated using equation 3.1. Firstly, the content of the encapsulated OD was measured by TGA. Figure 4.12 showed the decomposition temperatures of dried PDVB/OD microcapsules prepared by microsuspension polymerization using conventional and PIE methods for droplet generation compared to the bulk OD. It was found that the decomposition temperature ranges of the encapsulated OD in PDVB/OD prepared using both conventional and PIE methods were closed to that of bulk OD (140-300°C) as shown in Table 4.5. From these results, the contents of the encapsulated OD were 51 and 39 % for PDVB/OD microcapsules prepared using the PIE and

conventional, respectively. Based on monomer and OD ratio (1:1) in the recipes, the OD contents represented that low encapsulation efficiency was obtained in the case of conventional method whereas PIE method represented high efficiency and closed to the ideal (50 %) content.

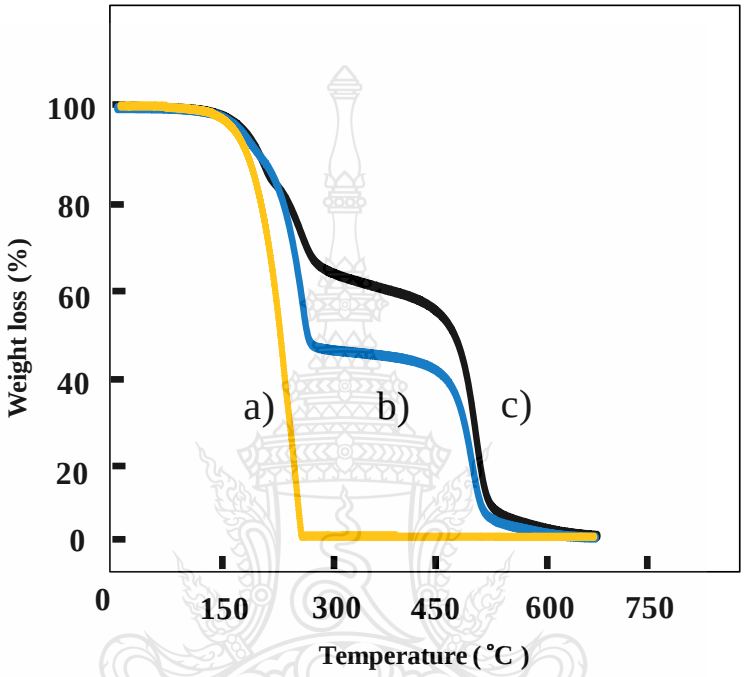


Figure 4.12 TGA thermograms (scanning rate 5 ˚C/min) of (a) bulk OD, dried PDVB/OD microcapsules prepared by the microsuspension polymerization using PIE (b) and conventional (c) methods for droplets generation

Table 4.5 TGA data of bulk OD, dried PDVB/OD microcapsules prepared by the microsuspension polymerization of DVB:OD (wt %); 50:50 using PIE and conventional methods for droplets generation

	Degradation interval (˚C)	**Weight loss (%)**
a) OD	140-300	100
b) PDVB/OD (PIE)	130-290 (1^{st} step)	51
	290-650 (2^{nd} step)	47
c) PDVB/OD (conventional)	130-310 (1^{st} step)	39
	310-650 (2^{nd} step)	52

The latent heats of the encapsulated OD in dried PDVB/OD microcapsules were measured with DSC as shown in Fig. 4.13. After calculation using equation 3.1, the H_m (189.1 J/g-OD) and H_c (192.7 J/g-OD) values of the encapsulated OD of PIE were closed to those of the bulk OD (233.3 and 233.7 J/g for H_m and H_c, respectively). In the case of conventional, H_m (152.1 J/g-OD) and H_c (152.7 J/g-OD) values were more lower than those of the bulk OD (Table 4.6).

The phase transition temperatures of PIE showed that the onset T_m of the encapsulated OD (22.6 °C) was similar with bulk OD (22.7 ˚C). On the other hand, T_c shifted greatly from the original value (26.3 ˚C) to a lower temperature (12.4 ˚C). This occurrence of supercooling of PCM capsules prepared by monomer polymerization was similar with the other reports [18, 19, 58]. Therefore, the prepared PDVB/OD microcapsules (approximately 2 μm with a narrow PSD) significantly increased of the total surface area [59], which could be applied for energy storage applications.

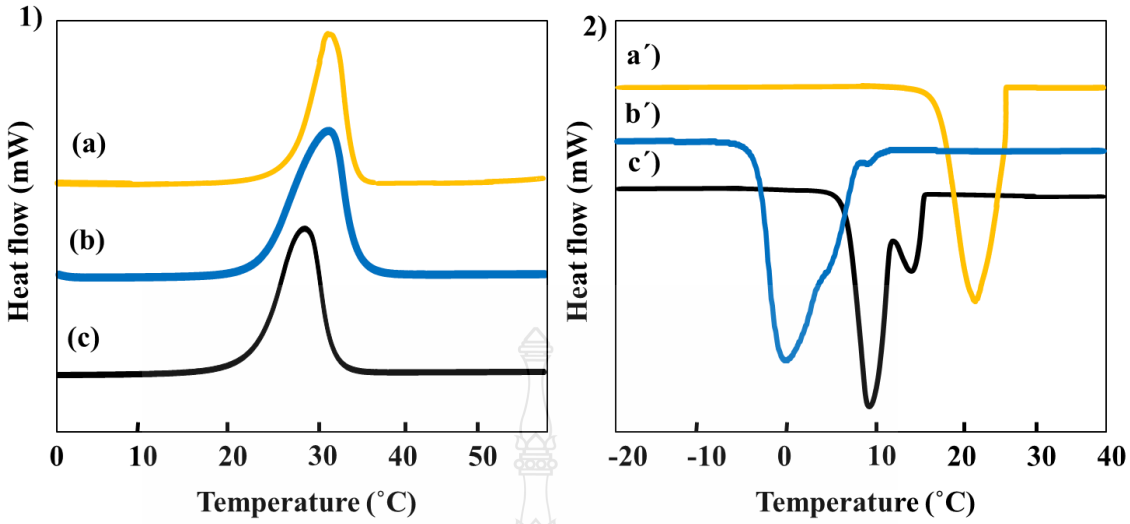


Figure 4.13 DSC thermograms (scanning rate 5˚C/min) of heating (1) and cooling (2) curves: (a, a´) bulk OD and encapsulated OD in dried PDVB/OD microcapsules using PIE (b, b´) and conventional (c, c´) methods

Table 4.6 Thermal properties of bulk OD, dried PDVB/OD microcapsules prepared by the microsuspension polymerization of DVB:OD (wt %); 50:50 using PIE and conventional methods for droplets generation

	Latent heats		**Transition temperatures**			
	H_m **(J/g-OD)**	H_c **(J/g-OD)**	T_m **(˚C)**		T_c **(˚C)**	
			Start point	**Peak point**	**Start point**	**Peak point**
a) OD	233.1	233.7	22.7	31.7	21.1	14.4
b) PIE	189.1	192.7	22.6	30.1	12.4	0.4
c) Conventional	152.1	152.7	18.0	27.3	17.1	9.7

4.2 Preparation of P(DVB-MMA)/OD microcapsules by microsuspension polymerize- tion using PIE for monomer droplet generation

In the previous part, although the encapsulation efficiency of OD in PDVB/OD microcapsule was high, the latent heats of the encapsulated OD were still different from those of the pure OD. The different of the latent heats would from the incomplete phase separation between OD core and PDVB shell. DVB monomer is quite hydrophobicity. Therefore PDVB is difficult to separate form OD after polymerization. To improve the phase separation, an increase in the polarity of polymer shell as in the case of PDVB/HD using the copolymerization of acrylic monomer [19] was carried out.

Therefore in this work, we tried to improve the latent heats of the encapsulated OD by copolymerization of DVB with hydrophilic monomer as MMA. Using the same procedure of the previous part, the copolymer P(DVB-MMA)/OD microcapsules then prepared by microsuspension polymerization using PIE for monomer droplet generation as shown in Fig. 3.1 and 3.3.

4.2.1 The study of the aqueous phase additional rate

It is well known that MMA monomer is high water solubility. The monomer droplets of the copolymer microcapsules would be more difficult to control both colloidal stability and PSD than those of PDVB/OD microcapsules. The monomer droplets were firstly prepared by PIE (Fig. 3.1) with various aqueous phases additional rates (2, 4 and 8 mL/min) and then copolymerized by microsuspension process (Fig. 3.3). As shown in the Table 4.7 and Fig. 4.14, the particle size diameter and PSD decreased with the decrease in the aqueous phase additional rate. In the case of 2 mL/min, PVA in oil phase have enough time to unity diffuse to adsorb on the oil-aqueous interface giving the smallest (d_w = 3.19 and d_n = 3.14 μm) and the narrowest PSD (d_w/d_n = 1.02). In the case of higher additional rate (4 and 8 mL/min), the PVA diffusion would disunity resulting in larger diameter and broader PSD (d_w = 5.66, d_n = 5.21 μm and d_w = 5.87, d_n = 5.40 μm for 4 and 8 mL/min, respectively).

Table 4.7 Weight- and number average diameters and particle size distribution[a] of P-(DVB-MMA)/OD[b] microcapsules prepared by microsuspension polymerize-tion with various additional rates of an aqueous phase at 24 h

Additional rate (mL/min)	Conversion (%)	d_w (nm)	d_n (nm)	d_w/d_n
2	69	3.19	3.14	1.02
4	65	5.66	5.21	1.09
8	65	5.87	5.40	1.09

[a] Measured by DLS

[b] DVB:MMA (wt %): 50:50

However, in all cases, good colloidal stability emulsions containing less amount of the coagulated particles were obtained. Most of P(DVB-MMA)/OD microcapsules floated on the top of the reactor whereas only small amount of the unencapsulated OD particles dispersed in the aqueous medium as shown in Fig. 4.15. In addition, the nonspherical core-shell microcapsules (Fig. 4.16) with the smooth outer surface (Fig. 4.17) were clearly observed in all cases. The OM and SEM data of those conditions accorded with the DLS that in the case of 2 mL/min of the additional rate, the smallest and the narrowest in particle size and PSD, respectively, were formed. Therefore, it was selected for co-monomer (DVB-MMA) droplets preparation and polymerized by microsuspension polymerization process.

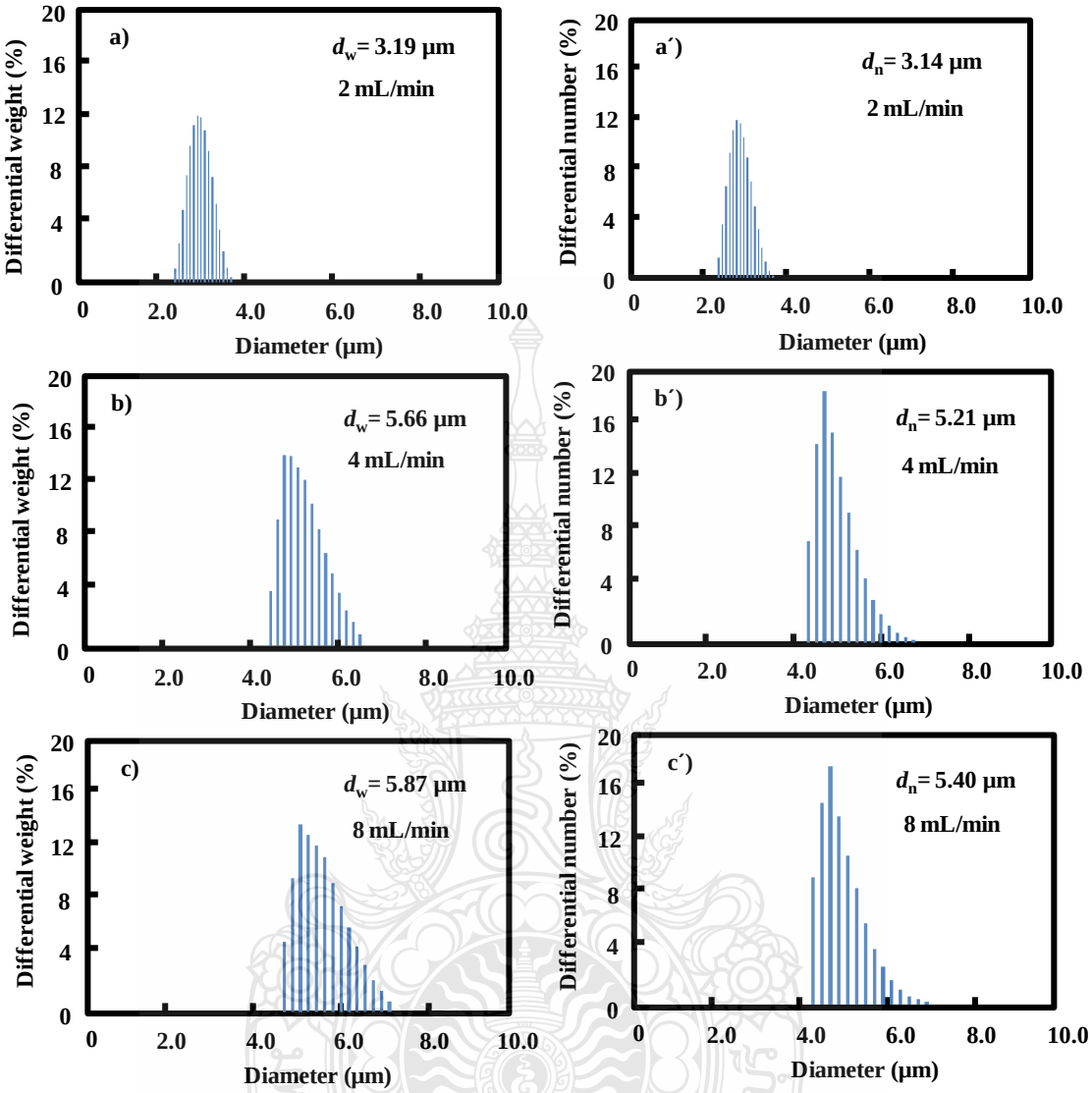


Figure 4.14 Weight- (d_w) and number (d_n) average diameters of P(DVB-MMA)/OD microcapsules using monomer ratio of DVB:MMA (wt %) at 50:50. The monomer droplets generated by PIE at the various additional rates: (a, a´) 2; (b, b´) 4 and (c, c´) 8 according to Table 4.7

Figure 4.15 The suspension photos of P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB: MMA (wt %) (50:50) at various additional rates (mL/min): a) 2; b) 4 and c) 8

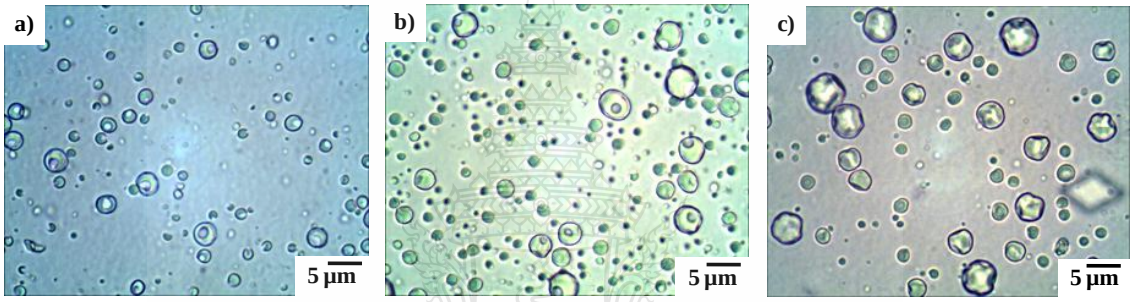


Figure 4.16 The optical micrographs of P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB: MMA (wt %) (50:50) at various additional rates (mL/min): a) 2; b) 4 and c) 8

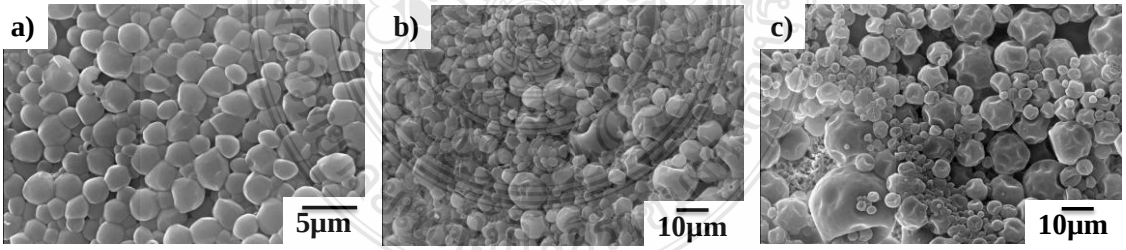


Figure 4.17 SEM micrographs of P(DVB-MMA)/OD microcapsules prepared by micro- suspension polymerization of DVB: MMA (wt %) (50:50) at various additional rates (mL/min): a) 2; b) 4 and c) 8

4.2.2 The study of the surfactant concentration

The P(DVB-MMA)/OD microcapsules obtained from the optimal condition in the previous part represented nonspherical particles. To clarify the formation of such particle, PVA dissolved in oil phase at various concentrations with and without SDS in the aqueous phase (Table 3.3) were studied. The produced P(DVB-MMA)/OD microcapsule suspensions of all conditions were shown in Fig. 4.18.

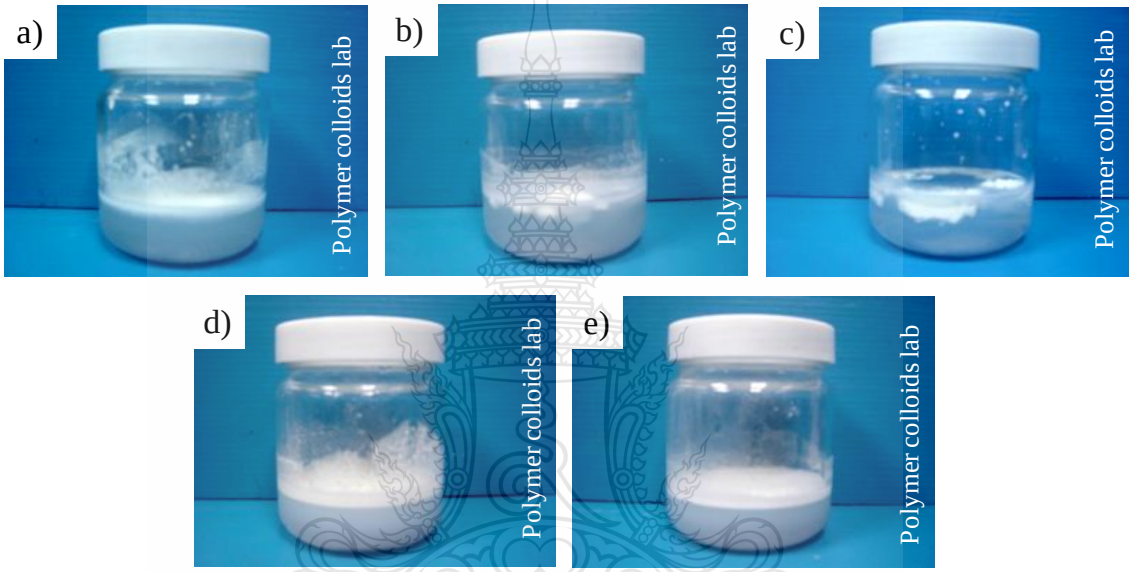


Figure 4.18 The suspension photos of P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB:MMA (wt %) (50:50) at various PVA (SDS) concentrations (wt %): a) 1 (0); b) 0 (0.1); c) 1 (0.1); d) 3 (0) and e) 3 (0.1) at aqueous phase additional rates of 2 mL/min at 24 h according to Table 3.3

In the case of using individual surfactant as 1 wt % of PVA in oil phase (Fig. 4.18a) and 0.1 wt % of SDS in aqueous medium (Fig. 4.18b), most of particles coagulated due to insufficient surfactant to stabilize the particles. Although, using the cooperative between PVA (1 wt %) and SDS (0.1 wt %) in the same amount of the previous condition, the colloidal stability of the obtained particles was still low. In addition, it was found that using only 1 wt % of PVA the P(DVB-MMA)/OD represented spherical microcapsules (Fig. 4.18a) while the nonspherical microcapsule

(Fig. 4.18b) was obtained with the simultaneous utilization of PVA (1.0 wt %) and SDS (0.1 wt %). It seemed that the addition of SDS is the reason of the nonspherical particle formation.

Table 4.8 Weight- and number average diameters and particle size distribution [a] of P(DVB-MMA)/OD microcapsules prepared by microsuspension polymeriza- tion of (DVB-MMA)/OD droplets prepared by PIE of aqueous phase additional rate 2 mL/min at 24 h with various PVA (SDS) concentrations

PVA (SDS) (wt %)	**Conversion (%)**	d_h **(μm)**	d_w **(μm)**		d_n **(μm)**		d_w/d_n	
			Main	Minor	Main	Minor	Main	Minor
3 (0.1)	69	3.69	3.19	-	3.14	-	1.02	-
3 (0)	46	8.85	5.63	9.79	4.65	8.69	1.21	1.13

[a] Measured with DLS

[b] PVA (SDS) concentration (wt %) of 1 (0), 0 (0.1) and 1 (0.1) are coagulant

However, to improve the colloidal stability of P(DVB-MMA)/OD microcapsule, PVA concentration was increased from 1.0 to 3.0 wt %. Moreover, the cooperative between PVA (3.0 wt %) and SDS (0.1 wt %) was studied as well. In the case of using only PVA (3.0 wt %), even though the stability of the particle was improved (Fig. 4.18d), some of the particle coagulation was still formed as shown in bimodal PSD (Table 4.8 and Fig. 4.20b). In general, the conventional suspension polymerization using homogenizer to generate monomer droplet, approximately 1 wt % PVA concentration in aqueous medium was used. The obtained particles showed high colloidal stability [17, 18, 36, 37]. The less stable of microcapsule prepared by PIE method using 1 wt % and 3 wt % of PVA could be explained by the partitioning experiment. The partitioning of PVA in the oil and aqueous phases was studied described in section 3.2.4. It was found that about 30% of PVA partitioned in the aqueous phase as shown in Table 4.9. This mean

that 0.3 wt % and 0.7 wt % of PVA existed in aqueous phase for 1 wt % and 3 wt % of PVA, respectively, in which they were lower than PVA concentration of the conventional suspension polymerization. This is the reason why the particle coagulation took place during the polymerization. However, the colloidal stability of P(DVB-MMA)/OD was successfully improved using the cooperative of PVA (3 wt %) and SDS (0.1 wt %) according with the optimal condition of the previous part. The droplet nucleation would mainly proceed in the case of using both surfactants while homogeneous nucleation seemed compete against droplet nucleation in the case of using only 3.0 wt % of PVA. Therefore, P(DVB-MMA)/OD microcapsules produced from both surfactants represented the smaller size (3.19 µm of d_w) than that (5.63 µm of d_w) of using only PVA (Table 4.8). Moreover, monomodal (Fig. 4.20a and a´) and bimodal (Fig. 4.20b and b´) PSDs were observed for using both surfactants and only PVA, respectively.

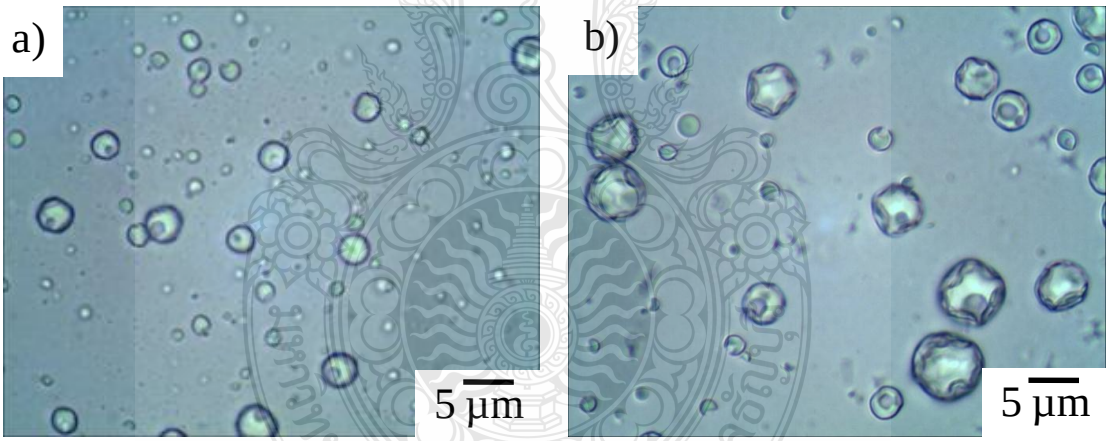


Figure 4.19 The optical micrographs of P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB: MMA (wt %) (50:50) using PVA (SDS) at various concentrations (wt %): a) 3 (0.1) and b) 3 (0) at the additional rate of 2 mL/min at 24 h according to Table 4.8

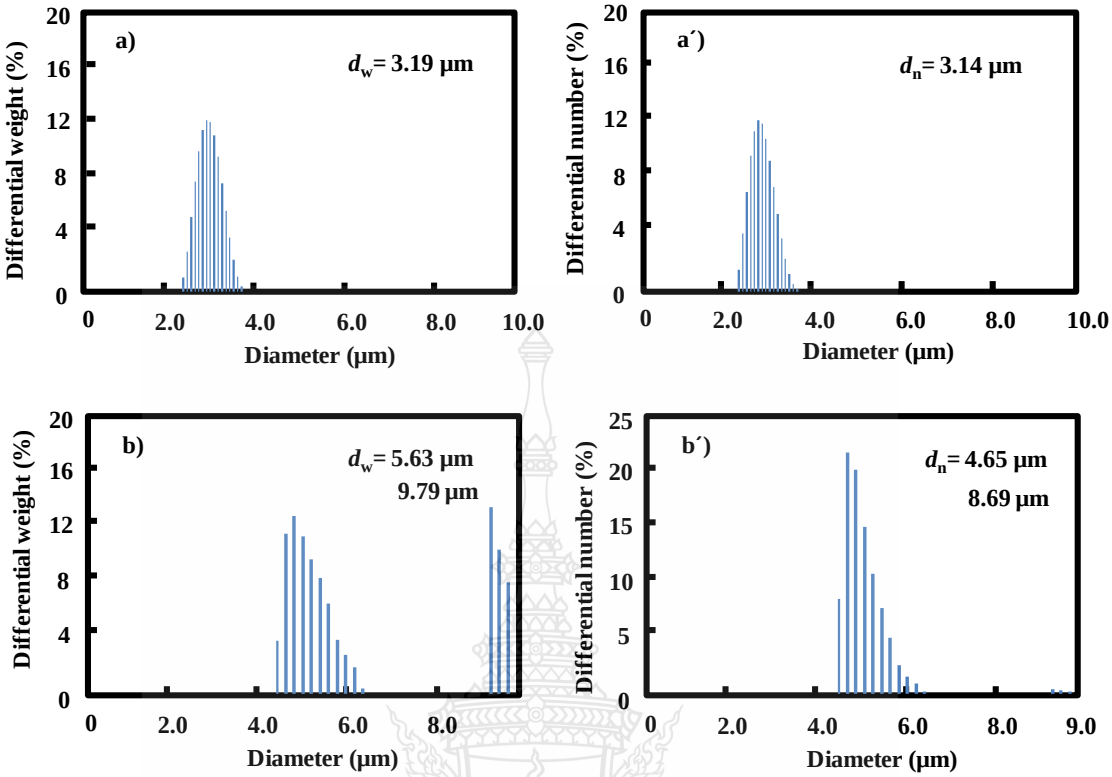


Figure 4.20 Weight- (d_w) and number (d_n) average diameters of P(DVB-MMA)/OD microcapsules using monomer ratio of DVB:MMA (wt %) at 50:50. The monomer droplets generated by PIE at various PVA (SDS) concentrations (wt %): (a, a´) 3 (0.1) and (b, b´) 3 (0) using additional rate of 2 mL/min at 24 h according to Table 4.8

These results indicated that the preparation of P(DVB-MMA)/OD microcapsules by microsuspension polymerization using monomer ratio of 50:50 (DVB:MMA) and 3 wt % of PVA and 0.1 wt % of SDS in oil and aqueous phases, respectively, was the optimal condition. The particle formation was mainly formed via droplet nucleation as the monomer droplets/polymer particles size were almost the same during the polymerization (Table 4.10 and Fig. 4.21). Moreover, the microcapsules had high colloidal stability in which only monomodal PSDs (Fig. 4.22) were observed throughout the polymerization.

Table 4.9 Partitioning of polyvinyl alcohol dispersed in oil and water phases were respectively 1 and 3 wt % of PVA

Phase	PVA (wt %)	
	1	**3**
Oil (wt %)	0.7	2.3
Aqueous (wt %)	0.3	0.7

Table 4.10 Conversions, (DVB-MMA)/OD droplet sizes and P(DVB-MMA) particle sizes[a] at various times during microsuspension polymerization of DVB:MMA (wt %) at 50:50 (PIE, additional rate of 2 mL/min) of PVA (SDS) concentration (wt %) at 3 (0.1) of the recipe shown in Table 3.3

Time (h)	Conversion (%)	d_h (μm)	d_w (μm)	d_n (μm)	d_w/d_n
0	-	4.47	2.12	2.09	1.01
1	54	4.36	3.29	3.23	1.02
3	60	3.55	2.88	2.82	1.02
8	68	3.36	2.42	2.39	1.01
24	69	3.65	3.19	3.14	1.02

[a] Measured by DLS; d_h is hydrodynamic particle diameter

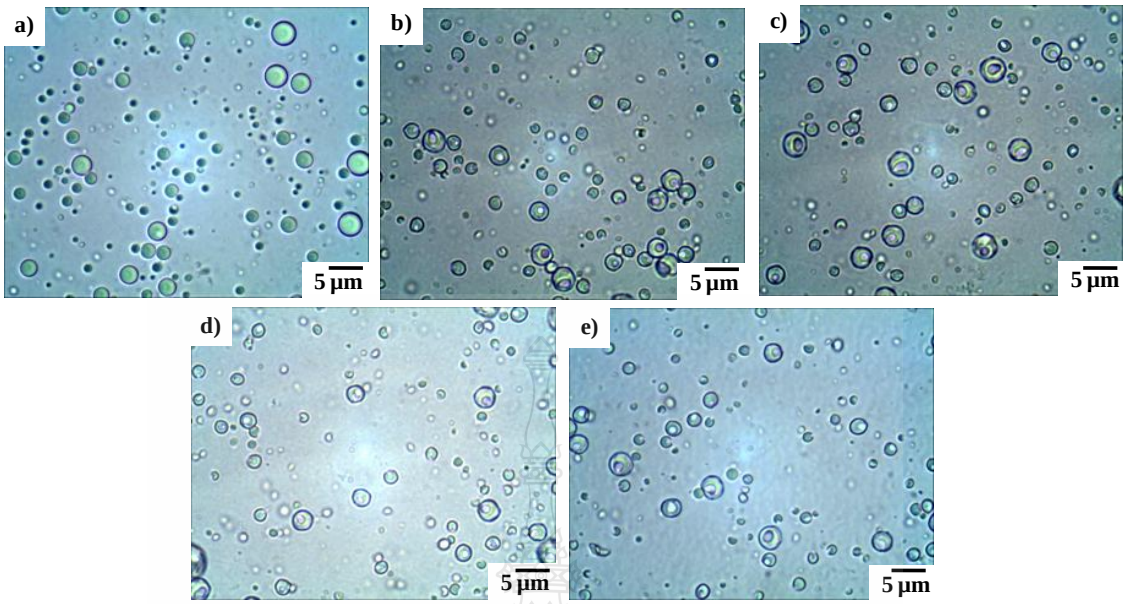


Figure 4.21 Optical micrographs of P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB:MMA (wt %) (50:50) at the additional rate of 2 mL/min. Polymerization times (h): a) 0; b) 1; c) 3; d) 8 and e) 24

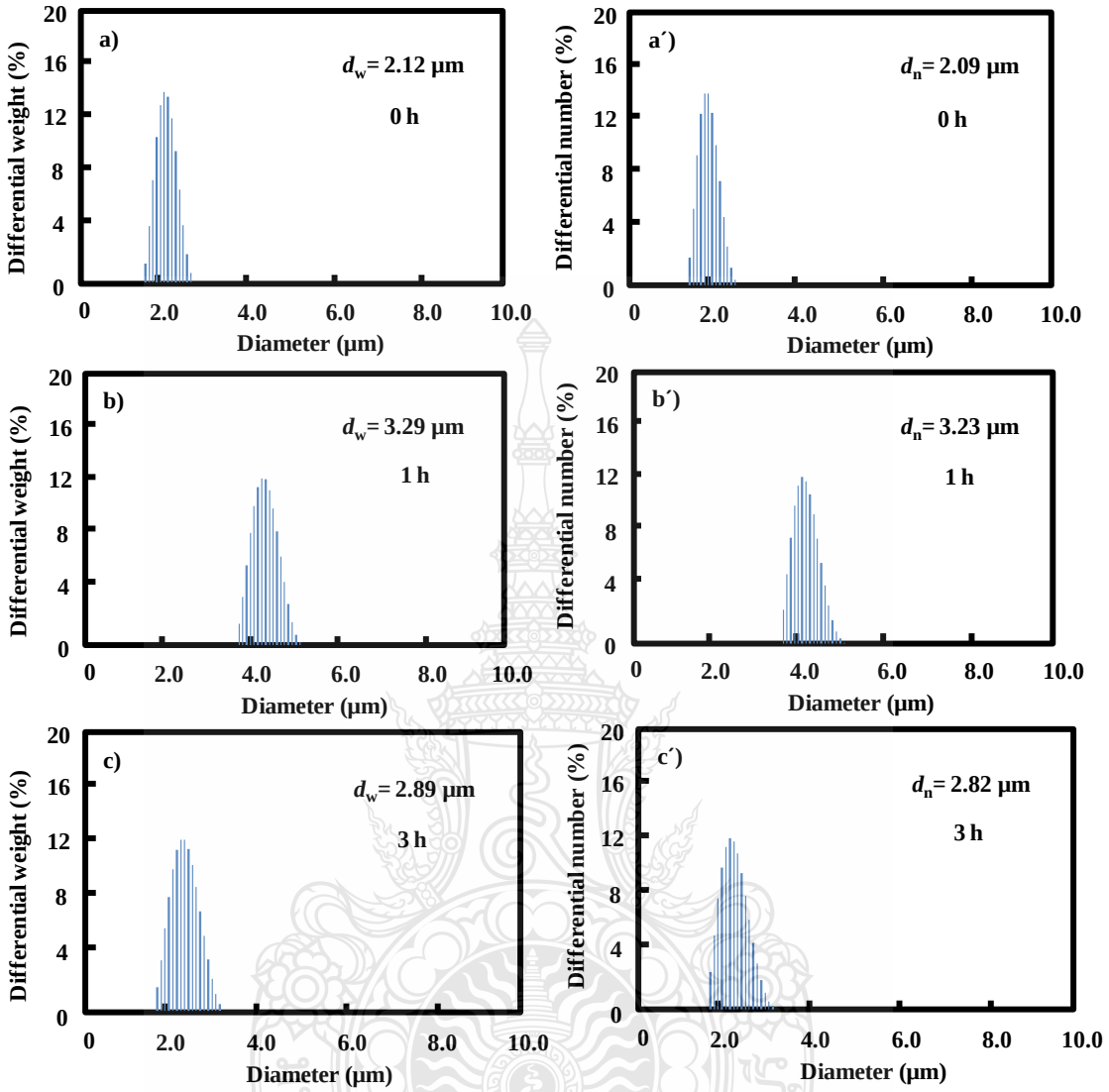


Figure 4.22 Weight- (d_w) and number (d_n) average diameters of P(DVB-MMA)/OD microcapsules using DVB:MMA (wt %) at 50:50 generated by PIE at the PVA (SDS) concentration (wt %) 3 (0.1) and additional rate of 2 mL/min. Polymerization times (h): (a, a´) 0; (b, b´) 1; (c, c´) 3; (d, d´) 8 and (e, e´) 24

(Fig. 4.22 continued)

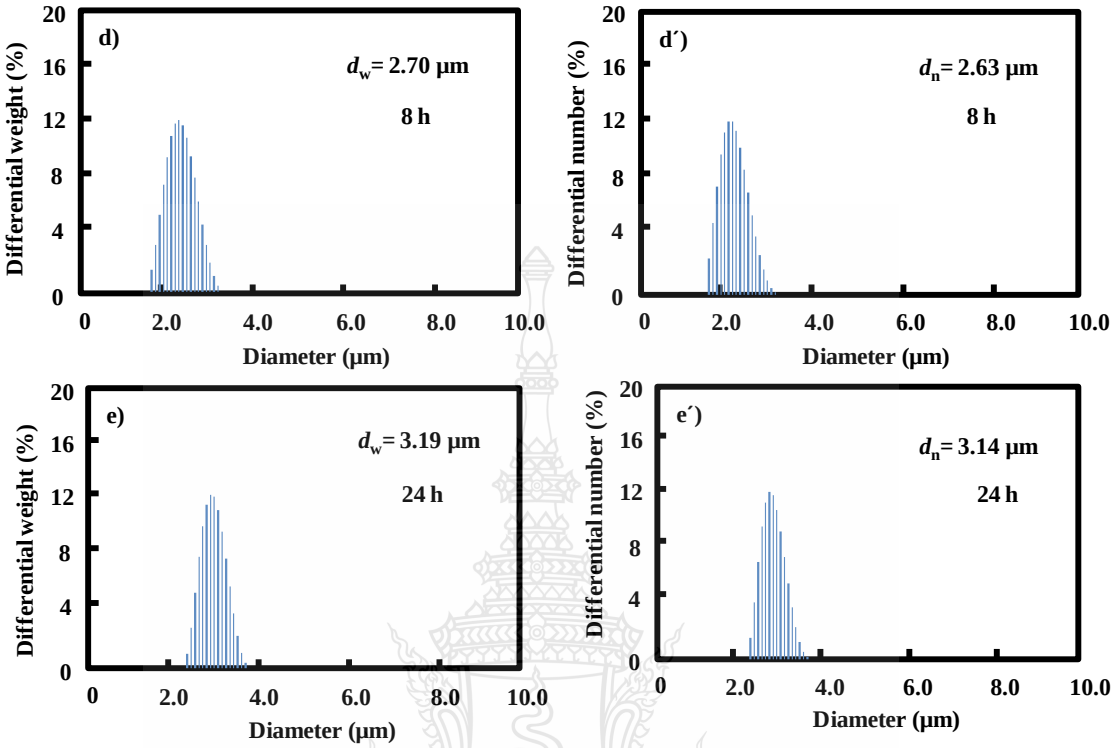


Figure 4.22 Weight- (d_w) and number (d_n) average diameters of P(DVB-MMA)/OD microcapsules using DVB:MMA (wt %) at 50:50 generated by PIE at the PVA (SDS) concentration (wt %) 3 (0.1) and additional rate of 2 mL/min. Polymerization times (h): (a, a´) 0; (b, b´) 1; (c, c´) 3; (d, d´) 8 and (e, e´) 24

4.2.3 The study of DVB:MMA ratio

As explained in the previous part, the latent heats of the encapsulated OD was able to be improved by increase in the polarity of the polymer shell. We have successfully prepared P(DVB-MMA)/OD microcapsules at the DVB:MMA ratio of 50:50. Using the optimal condition, the content of MMA was increased from 50 % to 70 % in order to improve the latent heats. It is well known that MMA is high water solubility [64]. Thus, the increase of MMA amount may raise the homogeneous nucleation in aqueous medium in which it was the main reason to reduce the

encapsulation efficiency and particle stability. Therefore, the particle formation during the polymerization was studied as well.

Table 4.11 Conversions, (DVB-MMA)/OD droplet sizes and P(DVB-MMA) particle sizes[a] at various times during microsuspension polymerization of DVB:MMA (wt %) at 30:70 (PIE, additional rate of 2 mL/min)

Time (h)	Conversion (%)	d_h (μm)	d_w (μm)	d_n (μm)	d_w/d_n
0	-	4.43	2.94	2.87	1.03
1	55	4.89	3.56	3.47	1.03
3	59	4.54	3.45	3.39	1.02
8	66	3.82	3.17	3.09	1.03
24	67	5.08	3.80	3.75	1.02

[a] Measured by DLS; d_h is hydrodynamic particle diameter

The particle size of the obtained P(DVB-MMA)/OD microcapsule was about 3-4 μm (Table 4.11) with a monomodal PSD (Fig. 4.23) throughout the polymerization. These indicated that the polymerization was mainly taken place in monomer droplet as in the case of 50:50 of DVB:MMA. In addition, the microcapsules contained multident in their surfaces. The core-shell microcapsules were clearly observed as shown in Fig. 4.24. The particle shape seemed similar to that of P(DVB-MMA)/OD microcapsules using 50:50 of DVB:MMA.

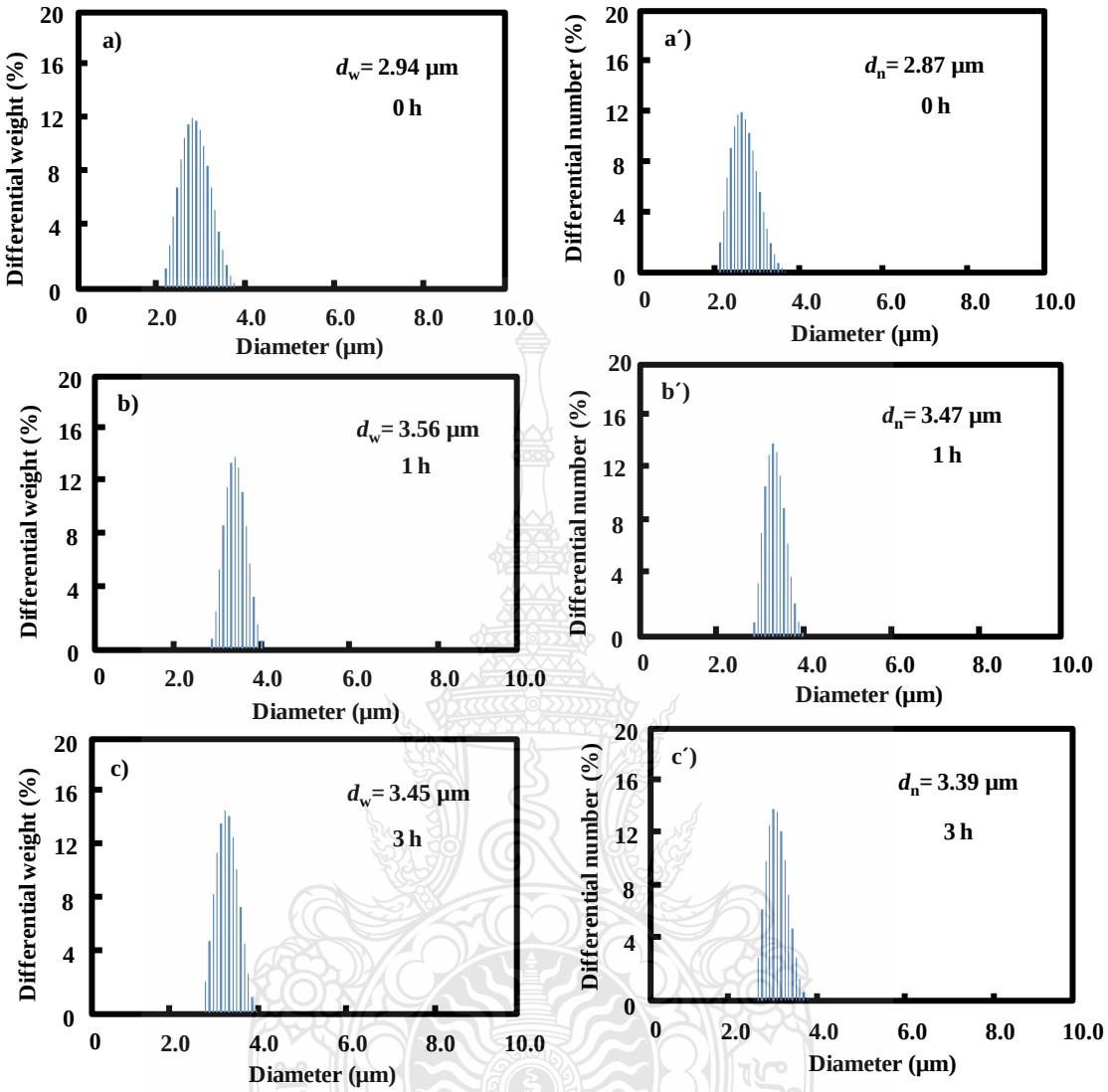


Figure 4.23 Weight- (d_w) and number (d_n) average diameters of P(DVB-MMA)/OD microcapsules using DVB:MMA (wt %) at 30:70 generated by PIE at the PVA (SDS) concentration (wt %) 3 (0.1) and additional rate of 2 mL/min. Polymerization times (h): (a, a´) 0; (b, b´) 1; (c, c´) 3; (d, d´) 8 and (e, e´) 24

(Fig. 4.23 continued)

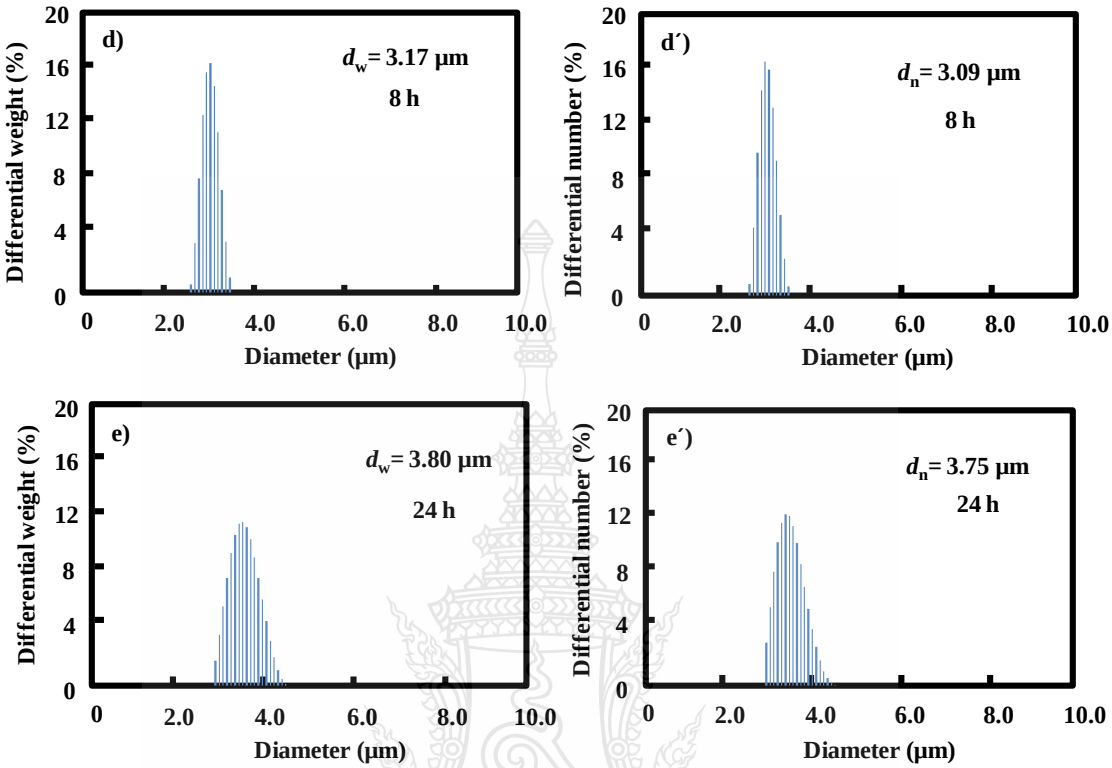


Figure 4.23 Weight- (d_w) and number (d_n) average diameters of P(DVB-MMA)/OD microcapsules using DVB:MMA (wt %) at 30:70 generated by PIE at the PVA (SDS) concentration (wt %) 3 (0.1) and additional rate of 2 mL/min. Polymerization times (h): (a, a´) 0; (b, b´) 1; (c, c´) 3; (d, d´) 8 and (e, e´) 24

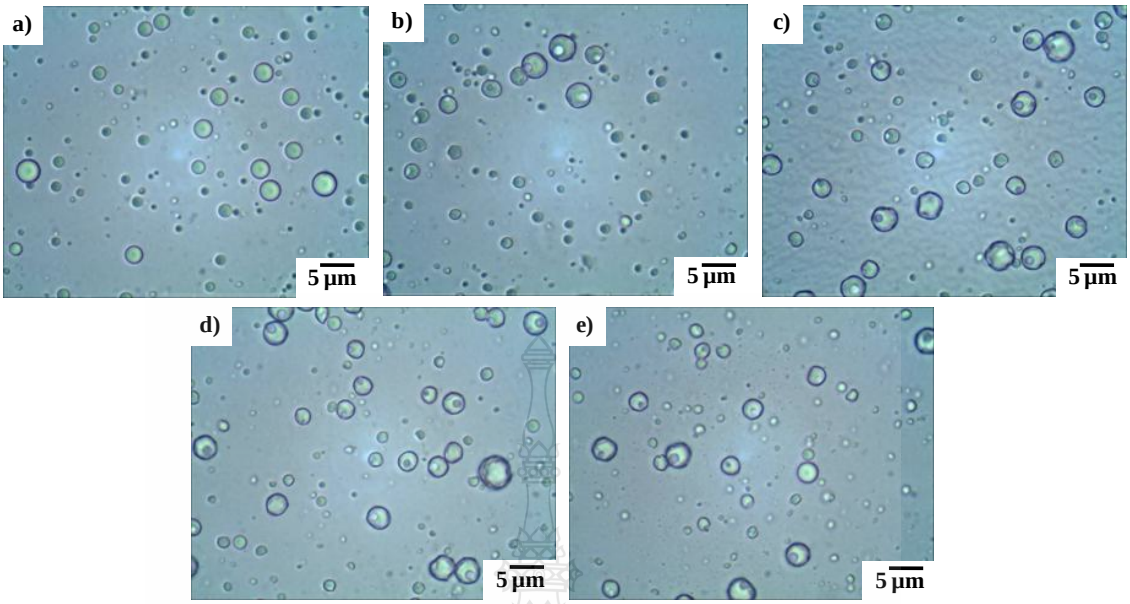


Figure 4.24 Optical micrographs of P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB:MMA (wt %) (30:70) at the additional rate of 2 mL/min. Polymerization times (h): a) 0; b) 1; c) 3; d) 8 and e) 24

4.2.4 Thermal properties of the encapsulated OD in P(DVB-MMA)/OD microcapsules

Similar to part 4.1, the thermal properties of bulk OD, DVB:MMA (100:0), DVB:MMA (50:50) and DVB:MMA (30:70) were observed by TGA shown in Fig. 4.25. The latent heats (H_m and H_c) of the encapsulated OD inside P(DVB-MMA)/OD microcapsules in a unit of joules per gram of OD (J/g-OD) was calculated using equation 3.1. Firstly, the contents of the encapsulated OD were measured by TGA. Figure 4.25 showed the decomposition temperatures of dried P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization using DVB:MMA (100:0), DVB:MMA (50:50) and DVB:MMA (30:70) compared to the bulk OD. In Table 4.12, it was found that the decomposition temperatures range of bulk OD is 140-300 $^{\circ}$C in which closed to those of the encapsulated OD in P(DVB-MMA)/OD prepared using PIE technique. From these results, the content of encapsulated OD could be obtained which are 51, 63 and 59 % for P(DVB-MMA)/OD microcapsules using DVB:MMA at 100:0,

50:50 and 30:70, respectively. The OD contents represented that PIE technique gave high encapsulation efficiency for P(DVB-MMA)/OD microcapsule preparation, in which they closed to the calculation as shown in Table 4.13.

Table 4.12 TGA data of bulk OD and dried P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB:MMA (wt %) at 100:0, 50:50 and 30:70 of PIE with additional rate of 2 mL/min at 24 h

	Degradation interval (°C)	**Weight loss (%)**
a) OD	140-300	100
b) DVB:MMA (100:0)	130-290 (1^{st} step)	51
	290-650 (2^{nd} step)	47
c) DVB:MMA (50:50)	130-300 (1^{st} step)	63
	300-650 (2^{nd} step)	37
d) DVB:MMA (30:70)	135-315 (1^{st} step)	59
	315-600 (2^{nd} step)	36

Table 4.13 Loading and % encapsulation of microencapsulated OD in the microcapsules of DVB:MMA at 100:0, 50:50 and 30:70 prepared by the microsuspension polymerization after washing with 2-propanol

	Loading (wt %)		% Encapsulation[c]
	Experiment[a]	Calculation[b]	
1) DVB:MMA (100:0)	51	52	98
2) DVB:MMA (50:50)	63	60	105
3) DVB:MMA (30:70)	59	60	98

[a] TGA thermogram

[b] Calculated using the following equation:

Loading (wt %)= [A / {A + B (% Conversion - % Free polymer)/ 100}] x100

Where A and B are, respectively, weights of OD and monomer in the recipe shown in Table 3.1

[c] % Encapsulation= (% Loading experiment /Loading calculation) x 100

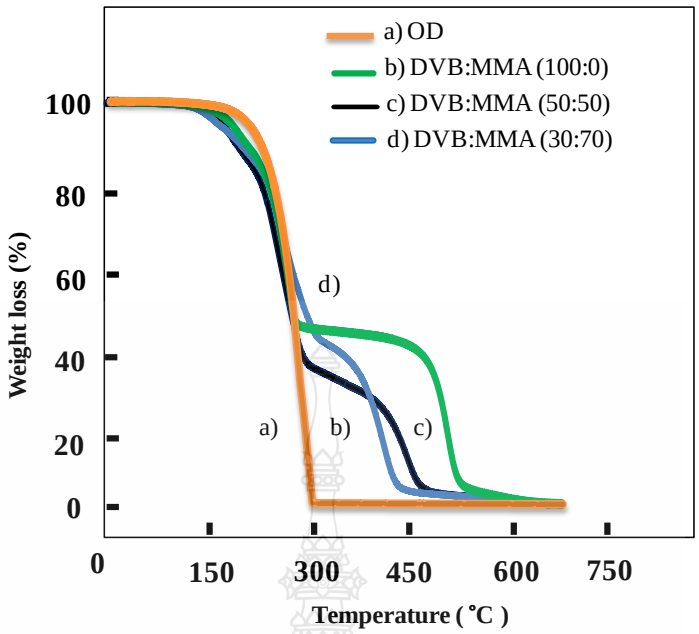


Figure 4.25 TGA thermograms (scanning rate 5°C/min) of a) bulk OD and dried P(DVB-MMA)/OD microcapsules of DVB:MMA (wt %): b) 100:0; c) 50:50 and d) 30:70

The obtained cooling/heating peak areas (Fig. 4.26) expressed the latent heats in the unit of Joules per 1g of sample. To compare the latent heats of the encapsulated OD in the microcapsules having different OD amount, the latent heats were expressed in a unit of Joules per 1g of OD as shown in Table 4.14 using equation 3.1. It was found that the latent heats (both H_m and H_c) increased with the MMA comonomer content. This supported our idea that the polarity of the polymer shell improved the encapsulated OD latent heats. In addition, at the ratio of 30:70 of DVB:MMA, the latent heats (H_m = 222 J/g-OD and H_c = 230 J/g-OD) closed to those of the bulk OD (H_m = 233 J/g-OD and H_c = 234 J/g-OD). This indicated that the obtained P(DVB-MMA)/OD microcapsules represented high performance of the heat storage materials which possible to apply in heat storage application.

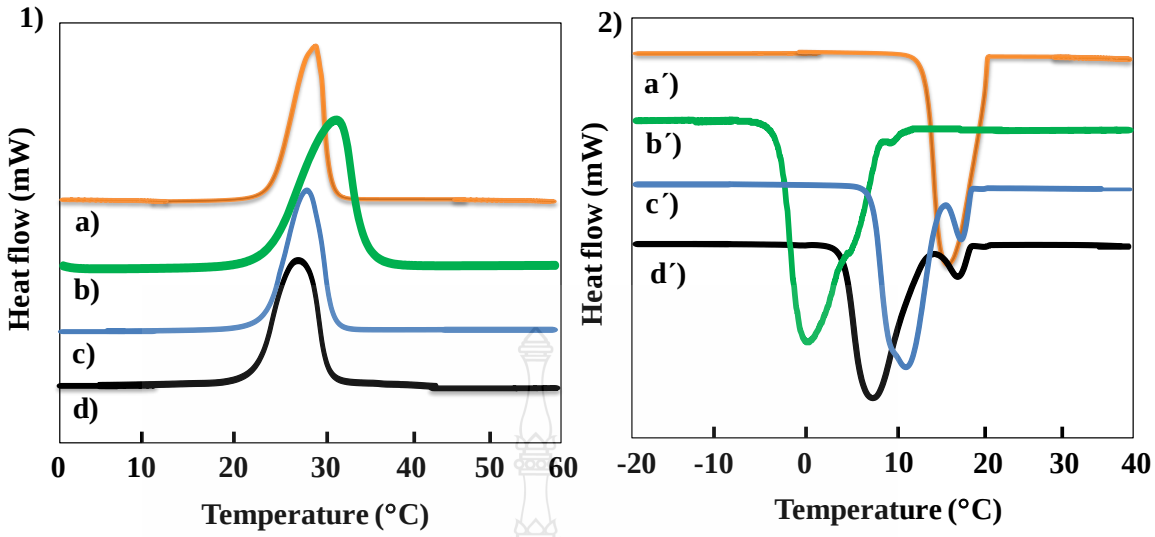


Figure 4.26 DSC thermograms (scanning rate 5°C/min) of heating (1) and cooling (2) curves: (a, a´) bulk OD and dried P(DVB-MMA)/OD microcapsules of various DVB:MMA (wt %): (b, b´) 100:0; (c, c´) 50:50 and (d, d´) 30:70

Table 4.14 Thermal properties of bulk OD and dried P(DVB-MMA)/OD microcapsules prepared by microsuspension polymerization of DVB:MMA (wt %) at 100:0, 50:50 and 30:70 with the additional rate of 2 mL/min at 24 h

	Latent heats		**Transition temperatures**			
	H_m **(J/g-OD)**	H_c **(J/g-OD)**	T_m **(°C)**		T_c **(°C)**	
			Start point	**Peak point**	**Start point**	**Peak point**
a) OD	233.1	233.7	22.7	31.7	21.1	14.4
b) DVB:MMA (100:0)	189.1	192.7	22.6	30.1	12.4	0.4
c) DVB:MMA (50:50)	218.2	221.4	22.4	28.0	12.7	6.7
d) DVB:MMA (30:70)	222.5	229.7	22.1	27.4	13.4	7.3

CHAPTER 5
CONCLUSIONS

5.1 Summary of experimental results

In this research, the preparation of DVB-based microcapsules encapsulated OD by microsuspension polymerization was studied using PIE for oil droplet generation compared with the conventional emulsification method. In the first step, using PIE, the PDVB/OD microcapsules were successfully prepared at 80°C for 24 h using PVA 3 wt % in oil phase and SDS 0.1 wt % in aqueous phase as surfactant and cosurfactant, respectively. The microcapsules were about 2 μm with narrower PSD and higher colloidal stability than those of the conventional emulsification method. The OM showed that OD was completely encapsulated with the PDVB shell. From SEM, regular spherical capsules with a dent and smooth outer surface were observed. The H_m and H_c of the encapsulated OD (189.1 and 192.7 J/g-OD, respectively) were lower than those of the bulk OD (H_m = 233.1 and H_c = 233.7 J/g-OD, respectively).

In the second step, the hydrophilic monomer as MMA was introduced in DVB-based microcapsules to improve latent heats of the encapsulated OD. Approximately 3 μm sized with a good colloidal stability microcapsules were successfully prepared by microsuspension polymerization of (DVB-MMA)/OD droplets produced by PIE using aqueous phase additional rate at 2 mL/min. However, the PSD was higher than that of PDVB/OD microcapsules due to the increase of hydrophilicity. The OM illustrated that OD was completely encapsulated with the P(DVB-MMA) shell. In the case of copolymer P(DVB-MMA)/OD microcapsules, the latent heats (H_m and H_c) were increased with the increase of MMA content from 50 to 70 wt % and closed to those of pure OD. Therefore, the prepared P(DVB-MMA)/OD microcapsules were able to used in heat storage applications, because of their large surface area and the excellent thermal properties.

List of Bibliography

[1] Y. Shin, D. Yoo, and K. Son, "Development of thermoregulating textile materials with microencapsulated phase change materials (PCM). II. Preparation and application of PCM microcapsules," *J. Appl. Polym. Sci.,* vol. 96, pp. 2005-2010, 2005.

[2] L. Sanchez, P. Sanchez, M. Carmona, A. Lucas, and J. Rodríguez, "Influence of operation conditions on the microencapsulation of PCMs by means of suspension-like polymerization," *Colloid Polym. Sci.,* vol. 286, pp. 1019-1027, 2008.

[3] J. F. Su, L. X. Wang, L. Ren, "Preparation and characterization of double-MF shell micro PCMs used in building materials," *J. Appl. Polym. Sci.,* vol. 93, pp. 1240-1251, 2005.

[4] S. Peng, A. Fuchs, and R. A. Wirtz, "Polymeric phase change composites for thermal energy storage," *J. Appl. Polym. Sci.,* vol. 93, pp. 1240-1251, 2004.

[5] J. S. Cho, A. Kwon, and C. G. Cho, "Microencapsulation of octadecane as a phase-change material by interfacial polymerization in an emulsion system," *Colloid Polym. Sci.,* vol. 280, pp. 260-266, 2002.

[6] M. M. Farid, A. M. Khudhair, S. A. K. Razack, and S. Al-Hallaj, "A review on phase change energy storage: materials and applications," *Energy Convers. Manage.,* vol. 45, pp. 1597-1615, 2004.

[7] M. Okubo, Y. Konishi, and H. Minami, "Production of hollow polymer particles by suspension polymerization," *Colloid Polym. Sci.,* vol. 276, pp. 638-642, 1998.

List of Bibliography (continued)

[8] P. Chaiyasat, A. Chaiyasat, W. Boontung, S. Promdsorn, and S. Thipsit, "Preparation and characterization of poly (divinylbenzene) microcapsules containing octadecane," *Mater Sci. Appl.,* vol. 2, pp. 1007-1013, 2011.

[9] A. Chaiyasat, C. Waree, K. Songkhamrod, P. Sirithip, V. Voranuch, P. Chaiyasat, "Preparation of polydivinylbenzene/natural rubber capsule encapsulating octadacane: Influence of natural rubber molecular weight and content," *Express Polym Lett,* vol. 6, pp. 70-77, 2012.

[10] D. Supatimusro, S. Promdsorn, S. Thipsit, W. Boontung, P. Chaiyasat, A. Chaiyasat, " Poly(divinylbenzene) microencapsulated octadecane for use as a heat storage material: influences of microcapsule size and monomer/octadacane ratio," *Polym. Plast. Technol. Eng.,* vol. 51, pp. 1167-1172, 2012.

[11] P. Sanchez, M. V. Sanchez-Fernandez, A. Romero, J. F. Rodriguez, L. Sanchez-Silva, "Development of thermo-regulating textiles using paraffin wax microcapsules," *Thermochim. Acta,* vol. 498, pp. 16-21, 2010.

[12] L. Sanchez-Silva, J. F. Rodriguez, A. Romero, P. Sanchez, "Preparation of coated thermo-regulating textiles using rubitherm-RT31 microcapsules," *J. Appl. Polym Sci.,* vol. 124 pp. 4809-4818, 2012.

[13] L. Sanchez-Silva, J. F. Rodriguez, A. Romero, A. M. Borreguero, M. Crmona, P. Sanchez, "Microencapsulation of PCMs with a styrene-methyl methacrylate copolymer shell by suspension-like polymerization," *Chem. Eng.*, vol. 157, pp. 216-222, 2010.

List of Bibliography (continued)

[14] M. You, X. Wang, X. Zhang, L. Zhang, J. Wang, "Microencapsulated n-octadacane with styrene-divinylbenzene co-polymer shells," *J. Polym. Res,* vol. 18, pp. 49-58, 2011.

[15] X. Qiu, W. Li, G. Tang, "Fabrication and characterization of microencapsulated n-octadacane with different crosslinked methylmethacrylate-based polymer shells," *Sol. Energ. Mat. Sol. C.,* vol. 98, pp. 283-293, 2012.

[16] L. Sanchez-Silva, J. Tsavalas, D. Sundberg, P. Sanchez, J.F. Rodriguez, "Synthesis and characterization of paraffin wax microcapsules with acrylic-based polymer shells," *Ind. Eng. Chem. Res.,* vol. 49, pp. 12204-12211, 2012.

[17] L. Sanchez, E. Lacasa, M. Carmona, J. F. Rodriguez, P. Sanchez, "Applying an experimental design to improve the characteristics of microcapsules containing phase change materials for fabric uses," *Ind. Eng. Chem. Res.,* vol. 47, pp. 9783-9790, 2008.

[18] P. Chaiyasat, T. Suzuki, H. Minami, M. Okubo, "Thermal properties of hexadecane encapsulated in poly(divinylbenzene) particles," *J. Appl. Polym. Sci.,* vol. 112, pp. 3257-3266, 2009.

[19] P. Chaiyasat, Y. Ogino, T. Suzuki, H. Minami, M. Okubo, "Preparation of divinylbenzene copolymer particles with encapsulated hexadecane for heat storage application," *Colloid Polym. Sci.,* vol. 286, pp. 217-223, 2008.

[20] Y. Yip, C. Sang, E. Lorenceau, S. Wahl, M. Stoffel, D. E. Angelescu and R. Höhler, "A microfluidic technique for generating monodisperse submicron-sized drops," *RSC Adv.,* vol. 3, pp. 2330-2335, 2013.

List of Bibliography (continued)

[21] Y. Guo, P. B. Zetterlund, "Synthesis of nanosized (<20 nm) polymer particle by radical polymerization in miniemulsion employing in situ surfacetant formation," *Macromol. Rapid Commun.,* vol. 32, pp. 1669-1675, 2011.

[22] Y. Guo, P. B. Zetterlund, " Particle formation mechanism in radical polymerization in miniemulsion based on in situ surfactant formation without high energy homogenization," *Polymer,* vol. 52, pp. 4199-4207, 2011.

[23] Y. Guo, J. Lie, P. B. Zetterlund, "Nitroxide-mediated radical polymerization in miniemulsion on the basis of in situ surfactant formation without use of homogenization device," *Macromolecules,* vol. 43, pp. 5914-5916, 2010.

[24] F. Hansali, M. Wu, D. Bendedouch, E. Marie, "n-Butyl cyanoacrylate miniemulsion polymerization via the phase inversion composition method," *Coll. Surf. A,* vol. 393, pp. 133-138, 2012.

[25] S. Cheng, Y. Guo, P. B. Zetterlund, "Miniemulsion polymerization based on low energy emulsification with preservation of initial droplet identity," *Macromolecules,* vol. 43, pp. 7905-7907, 2010.

[26] Y. Guo, V. L. Teo, S. S. Ting, P. B. Zetterlund, "Miniemulsion polymerization based on in situ surfactant formation without high-energy homogenization: effects of organic acid and counter ion," *Polymer,* vol. 44, pp. 375-381, 2012.

[27] A. Abhat., "Low temperature latent heat thermal energy storage: heat storage materials," *Sol. Energy,* vol. 30, pp. 313–32, 1981.

[28] A. A. Robaidi, "Development of novel polymer phase change material for heat storage application " *Int. J. Mater. Sci. Appl.,* vol. 2, pp. 168-172 2013.

List of Bibliography (continued)

[29] D. Zhou, C. Y. Zhao, Y. Tian, "Review on thermal energy storage with phase change materials (PCMs) in building applications," *Appl. Energy,* vol. 92, pp. 593-605, 2012.

[30] B. IM., "Enhancing the thermal response of latent heat storage systems," *Int. J Energy Res.,* vol. 21, pp. 759-766, 1997.

[31] S. Hiran, Suwondo, A., Mansoori, G., "Characterization of alkanes and paraffin waxes for application as phase change energy storage medium " *Energ. Source,* vol. 16, pp. 117-128, 1994.

[32] D. Glew. G. A. Lane, "Heat of fusion system for solar energy storage. In: Proceedings of the workshop on solar energy storage subsystems for the heating and cooling of buildings," *University of Virginia: Charlothensville,* vol. 28, pp. 43–55, 1975.

[33] P. A. Prabhu, N. N. Shinde, Prof. Patil P.S., "Review of phase change materials for thermal energy storage applications," *Int. J. Eng. Res. Appl.,* vol. 2, pp. 871-875, 2012.

[34] G. A. Lane et. al., "Macro-encapsulation of PCM.," *Report no. ORO/5117-8. Midland, Michigan: Dow Chemical Company,* vol. 30, pp. 152-156, 1978.

[35] B. Zalba, J. M. Marín, L. F. Cabeza, and H. Mehling, "Review on thermal energy storage with phase change: materials, heat transfer analysis and applications," *Appl. Therm. Eng.,* vol. 23, pp. 251-283, 2003.

List of Bibliography (continued)

[36] C. Thies, "Microencapsulation," *In Kirk–Othmer Encyclopedia of Chemical Technology, 5th ed., John Wiley & Sons Inc., Hoboken,* vol. 16, pp. 438-463., 2006.

[37] P. L. Foris, R. W. Brown, P.S. Phillips, "Microencapsulation" *Capsule manufacture, US Patent.* vol. 4, pp. 100-103 1978.

[38] S. K. Ghosh, "Functional coatings and microencapsulation: a general perspective," *in: S.K. Ghosh (Ed.), Functional coatings: By polymer microencapsulation, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim,* vol. 3, pp. 1-28, 2006.

[39] S. Gschwander, P. Schossig H. M. Henning, "Micro-encapsulated paraffin in phase-change slurries," *Sol. Energ. Mater. Sol. C,* vol. 89, pp. 307-315, 2005.

[40] M. N. A. Hawlader, M. S. Uddin, and M. M. Khin, "Microencapsulated PCM thermal-energy storage system," *Appl. Energ.,* vol. 74, pp. 195-202, 2003.

[41] B. K. Green, "Pressure sensitive record material," *US Patent,* vol. 2, pp. 712-716, 1955.

[42] B. K. Green, S. Lowell, "Manifold record material," *US Patent,* vol. 2, pp. 730-734, 1956.

[43] B. K. Green, S. Lowell, "Oil-containing microscopic capsules and method of making them," *US Patent,* vol. 2, pp. 800-814, 1957.

List of Bibliography (continued)

[44] R. Abderrahmen, C. Gavory, D. Chaussy, S. Brianc, H. Fessi, M. N. Belgacem, "Industrial pressure sensitive adhesives suitable for physicochemical microencapsulation," *Int. J. Adhes. Adhes.* , vol. 31, pp. 629-633, 2011.

[45] S. Gouin, "Microencapsulation: industrial appraisal of existing technologies and trends," *Trends Food Sci. Technol.* , vol. 15, pp. 330-347, 2004.

[46] A. Gharsallaoui, G. Roudaut, O. Chambin, A. Voilley, R. Saurel, "Applications of spray–drying in microencapsulation of food ingredients: an overview," *Food Res. Int.* , vol. 40, pp. 1107-1121, 2007.

[47] M. Okubo, Y. Konishi, H. Minami, "Influence of the kind of end groups of polysterene on the production of hollow particles by suspension polymerization for divinylbenzene/toluene droplets dissolving them," *Colloid Polym. Sci.*, vol. 279, pp. 519-523, 2001.

[48] Y. Konishi, M. Okubo, H. Minami, "Phase seperation in the formation of hollow particles by suspension polymerization for divinylbenzene/toluene droplets dissolving polystyrene," *Colloid Polym. Sci.*, vol. 281, pp. 123-129, 2003.

[49] L. Sanchez-Silva, M. Carmona, A. de Lucas, P. Sanchez, J. Rodriguez, "Scale-up of a suspension-like polymerization process for the microencapsulation of phase change materials," *J. Microencapsul.*, vol. 27, pp. 583-593, 2010

[50] J. L. Salager, A. Forgiarini, L. Márquez, A. Peňa, A. Pizzino, M. P. Rodriguez, *et al.*, "Using emulsion inversion in industrial processes," *Adv. Colloid Interfac.*, vol. 108, pp. 259-272, 2004.

List of Bibliography (continued)

[51] P. Fernandez, V. Andre, J. Rieger, A. Kuhnle, "Nano-emulsion formation by emulsion phase inversion," *Colloid Surface A*, vol. 251, pp. 53-58, 2004.

[52] N. Anton, J.P. Benoit, and P. Saulnier, "Design and production of nanoparticles formulated from nano-emulsion templates -A review. ," *J. Control. Release*, vol. 128, pp. 188-199, 2008.

[53] V. Preziosi, A. Perazzo, S. Caserta, G. Tomaiuolo, S. Guido, "Phase inversion emulsification," *Chem. Eng. Trans.*, vol. 32, pp. 1585-1590, 2013.

[54] S. Sajjadi, "Nanoemulsion formation by phase inversion emulsification: on the nature of inversion," *Langmuir*, vol. 22, pp. 5597-5603, 2006.

[55] S. Sajjadi, F. Jahanzad, M. Yainneskis, "Catastrophic phase inversion of abnormal emulsions in the vicinity of the locus of transitional inversion," *Coll. Surf. A*, vol. 240, pp. 149-155, 2004

[56] A. Tan, A. Ziegler, B. Steinbauer and J. Seelig, "Thermodynamics of sodium dodecyl sulfate partitioning into lipid membranes," *Biophys. J.*, vol. 83, pp. 1547-1556, 2002.

[57] Y. Ai, Y. Jin, J. Sun and D. Wei "Microencapsulation of n-hexadecane as phase change material by suspension polymerization," *e-Polymers*, vol. 098, pp. 1-9, 2007

List of Bibliography (continued)

[58] X. X. Zhang, Y. F. Fan, X. M. Tao and K. L. Yick, "Fabrication and properties of microcapsules and nanocap-sules containing n-octadecane," *Mater. Chem. Phys*, vol. 88, pp. 300-307, 2004.

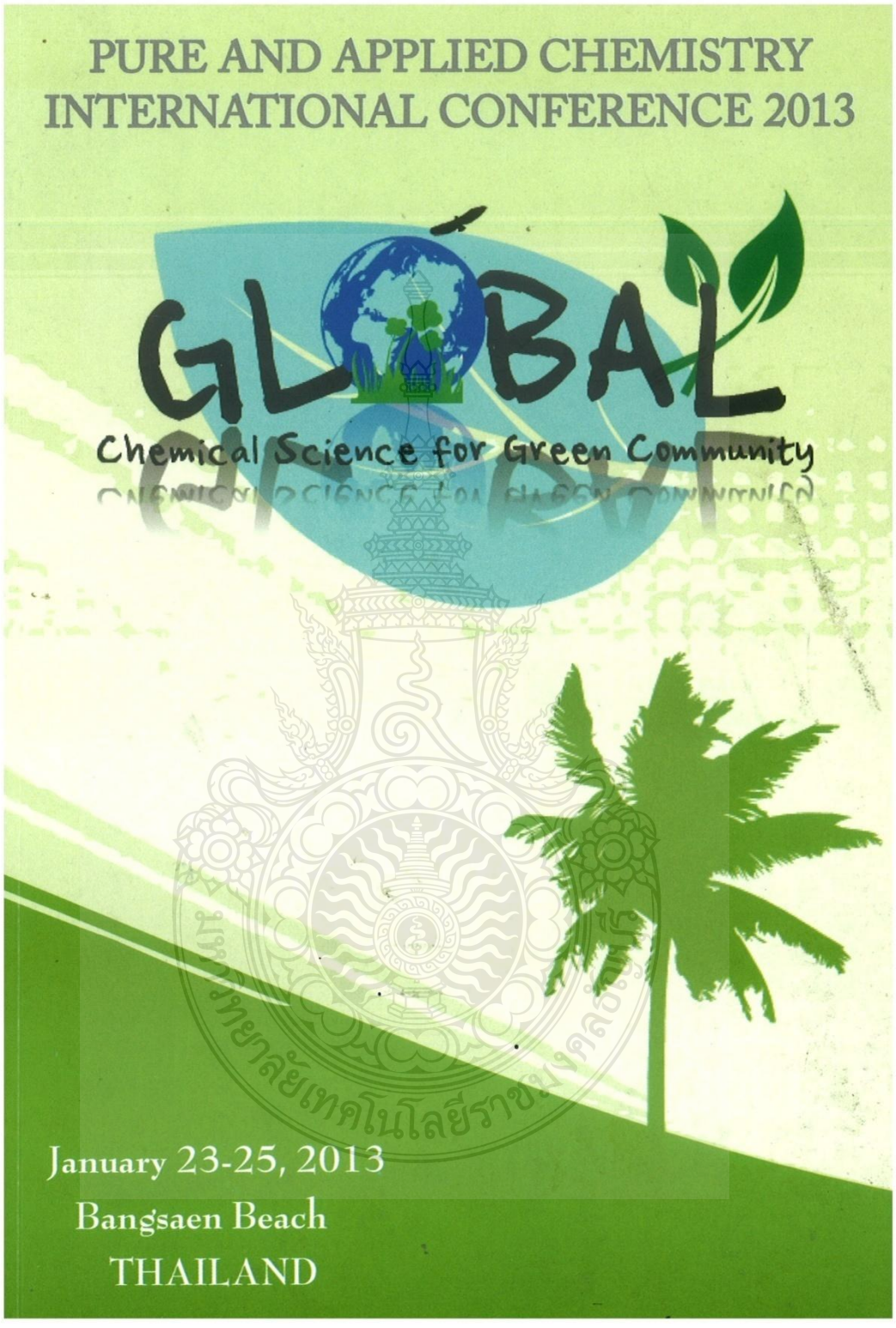
[59] P. Chaiyasat, Md. Z. Islam and A. Chaiyasat, "Preparation of poly(divinylbenzene) microencapsulated octadecane by microsuspension polymerization: oil droplets generated by phase inversion emulsification," *RSC Adv.*, vol. 3, pp. 10202-10207, 2013.

APPENDIX

APPENDIX A

POSTER PRESENTATION

PURE AND APPLIED CHEMISTRY INTERNATIONAL CONFERENCE 2013



POSTER PRESENTATIONS

Poster presentations will be held on at Room Pacific 4.

Poster Board

You will be provided with a poster board to mount/display your poster. The **Poster Size** is 100 centimeter (Height) by 80 centimeter (Width). Your Poster number will be indicated in the board. You will be provided with the material to mount your poster onto the board.

Setting Up and Removing Posters

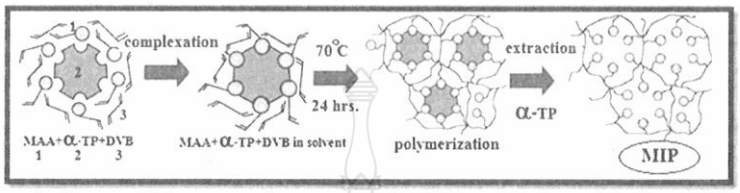
There are three poster sessions, **A**, **B** and **C**, the presenters are kindly requested to mount up and take off the posters following the appointed schedule;

Poster Presentation session/Date	**A** (23-Jan-2013)	**B** (24-Jan-2013)	**C** (25-Jan-2013)
Analytical Chemistry	ANC-P-001-057	ANC-P-058-097	
Biological / Biophysical Chemistry and Chemical Biology		BBC-P-001-029	
Bioinformatics		BIF-P-001	
Chemical Education		CHE-P-001-005	
Cosmetics		COS-P-001-007	
Environmental Chemistry	ENC-P-001-035		
Free radicals/ Antioxidants			FRA-P-001-015
Food safety and Food Chemistry	FSC-P-001-020		
Industrial Chemistry and Innovation		IIN-P-001-021	
Inorganic Chemistry	INC-P-001-021		
Material Sciences and Nanotechnology	MSC-P-001-052		MSC -P-053-111
Organic Chemistry and Medicinal Chemistry		OCM-P-001-033	OCM-P-034-079
Physical and Computational Chemistry		PCC-P-001-030	PCC-P-031-053
Polymer Chemistry	PMC-P-001-025	PMC-P-026-055	
Petroleum Chemistry and Catalysis		PTC-P-001-014	
Installation Date/Time 22-Jan-2013	16.00-20.00	24-Jan-2013	25-Jan-2013
23-Jan-2013	8.00-9.00	8.00-10.00	8.00-9.00
Display	14.00 - 18.30	13.00 - 18.30	9.00 - 10.10
Discussion	17.10 -18.30	17.10 - 18.30	9.00 - 10.10
Removable Date/Time	18.30-20.00	18.30-20.00	10.30-12.00

PMC P 003 PREPARATION OF MOLECULARLY IMPRINTED POLY (DIVINYLBENZENE-CO-METHACRYLIC ACID) PARTICLE BY PRECIPITATION POLYMERIZATION

M. Luttaprecha, P. Chaiyasat, A. Chaiyasat

Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Thailand



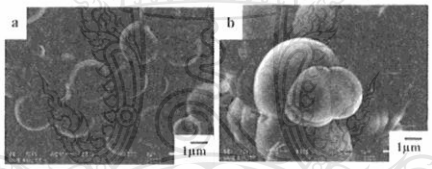
Schematic diagram of the preparation process of P(DVB-co-MAA) particles by precipitation polymerization

Keywords Vitamin E; Molecularly imprinted polymer; Precipitation polymerization

PMC P 004 PREPARATION OF POLYDIVINYLBENZENE/OCTADACANE MICROCAPSULE BY MODIFIED SUSPENSION POLYMERIZATION USING PHASE INVERSION EMULSIFICATION FOR MONOMER DROPLET GENERATION

Zahidul Islam, A. Chaiyasat and P. Chaiyasat

Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi,, Thailand



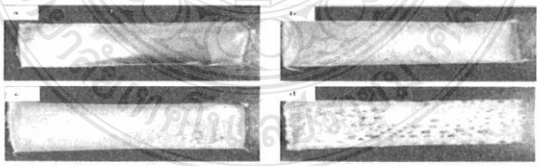
1SEM micrographs of PDVB/OD microcapsules prepared by the suspension polymerization of DVB/OD droplets generated by PIE (a) and conventional method (b)

Keywords Microencapsulation; Phase Change Material; Octadecane;

PMC P 005 PREPARATION OF POLY(L-LACTIC ACID)/SILVER NANOPARTICLE COMPOSITE FILM

W. Tawiya, S. Moonmangmee, A. Chaiyasat, P.Chaiyasat

Faculty of Science and Technology, RajamangalaUniversitr of Technology Thanyaburi, , Thailand



Photographs of PLLA/Ag film with various emulgen concentrations (% wt): a) 1; b) 2; c) 4 and d) 8

Keywords Poly(l-lactic acid); Silver nanoparticle; Water in oil emulsion

Preparation of polydivinylbenzene/octadacane microcapsule by modified suspension polymerization using phase inversion emulsification for monomer droplet generation

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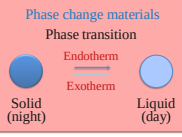
Introduction

Phase change materials (PCMs) are the materials that can store and release energy above their phase transitions. PCMs are attractive for many industrial applications such as air conditions of building, solar heat storage, thermal adaptable fibers and temperature-adaptable greenhouses [1]. Paraffin waxes are used as PCMs because they are nontoxic, non-corrosive, chemically inert and low cost. However, they have low thermal conductivity. To overcome this drawback, they require large surface areas. Therefore, in recent years, the encapsulation of these materials have been developed due to many advantages such as providing large heat transfer area and controlling the volume change of the storage materials as phase change occurs [2]. The microcapsules of paraffin are prepared by many techniques. One of the most famous technique is the polymerization using internal phase separation mechanism [3] such as suspension and miniemulsion polymerizations. However, they need high shear rate to generate the oil droplets resulting in high cost and energy expense [4]. Therefore, in this work, the PDVB/OD microcapsules are firstly prepared by suspension polymerization using phase inversion emulsification (PIE) for oil droplet generation with low shear rate.



Experimental

Table 1 Recipes for the preparation of PDVB/OD microcapsules by suspension polymerization[a] of DVB/OD droplets prepared by the mechanical stirring[b].

Ingredients[c]	Experiments	
	1	2
DVB (g)	5.0	5.0
OD (g)	5.0	5.0
BPO (g)	0.4	0.4
PVA (g)	3.0	3.0
SDS (g)	0.1	0.1
Water (g)	86.5	86.5

[a] 80°C, 24 hours, stirring rate at 200 rpm and 10 min N_2
[b] 500 rpm, 20 min
[c] Experiments 1 is PIE method and experiment 2 is conventional method for the monomer droplets preparation

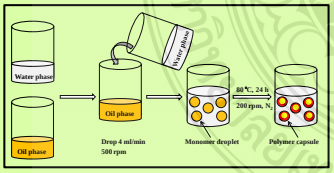


Fig. 1 Schematic of the preparation process of PDVB/OD microcapsules by suspension polymerization.

Results and Discussion

Table 2 Number, weight average diameters and particle size distribution [a] of PDVB/OD capsules prepared by suspension polymerization.

Experiments [b]	D_w[a](μm)	D_n[a](μm)	D_w/D_n
1	1.55	1.49	1.04
2	2.32	0.19	12.21

[a] Measured with DLS
[b] Experiments 1 and 2 according to the recipes of Table1

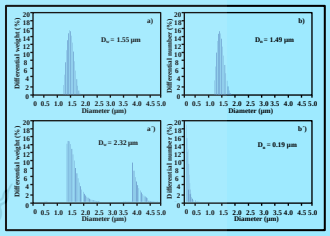


Fig. 2 Weight and number average diameters (D_w and D_n), respectively of (a, b) experiment 1 and (a´, b´) experiment 2 according to the recipes of Table 2.

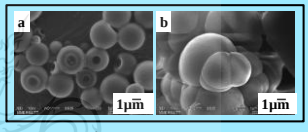


Fig. 3 SEM micrographs of PDVB/OD microcapsules prepared by the suspension polymerization of DVB/OD droplets generated by PIE (a) and conventional method (b)

Conclusions

The PDVB/OD microcapsules are successfully prepared by modified suspension polymerization using PIE for the monomer droplets generation. The PDVB/OD microcapsules using PIE gave much narrower particle size distribution (D_w/D_n = 1.04) than that of the conventional one (D_w/D_n = 12.21). Moreover, the capsules prepared by the conventional suspension polymerization represented bimodal PSD.

References

1. S. Peng, A. Fuchs, R.A. Wirtz, Polymeric phase change composites for thermal energy storage, J. Appl. Polym. Sci., 93 (2004) 1240-1251.
2. M.M. Farid, A.M. Khudhair, S.A.K. Razack, S. Al-Hallaj, A review on phase change energy storage: materials and applications, Energ Convers. Manage., 45 (2004) 1597-1615.
3. M. Okubo, Y. Konishi, H. Minami, Production of hollow polymer particles by suspension polymerization, Colloid Polym. Sc., 276 (1998) 638-642.
4. P. Chaiyasat, A. Chaiyasat, W. Boontung, S. Promdsorn, S. Thipsit, Preparation and Characterization of Poly(divinylbenzene) Microcapsules Containing Octadacane, Mater Sci Appl, 2 (2011) 1007-1013.

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