

CHAPTER II

EXPERIMENTAL

2.1 Chemicals

1. Methyl methacrylate monomer, commercial grade : Thai MMA Co., Ltd.
2. Butyl acrylate monomer, commercial grade : Atofina South East Asia Pte, Ltd.
3. Methacrylic acid monomer, commercial grade : Mitsubishi Rayon
4. Ammonium persulfate, commercial grade : Shanghai Ai Jian Reagent Works
5. Fatty alcohol ethoxylate sulfates : Cognis Thai Co., Ltd.
6. Alkylphenol ethoxylate sulfates : Cognis Thai Co., Ltd.
7. Fatty alcohol ethoxylates : Cognis Thai Co., Ltd.
8. Alkyl phenol ethoxylates : Dow Chemical Thailand Ltd.
9. Tertiary butyl hydroperoxide : Atofina South East Asia Pte, Ltd
10. Sodium formaldehyde sulfoxylate-B : Bruggemann Chemical
11. Texanol (2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate) : Eastman Chemical Singapore Pte, Ltd
12. Butyl cellosolve :Dow Chemical Thailand Ltd.
13. Ammonia solution 26% : Asian Chemical
14. Formaldehyde solution : TOA Dovechem Industries Co., Ltd.
15. Sodium Carbonate, commercial grade : Tianjin Bohai Chemical Industry United Import & Export Corporation
16. Sodium Chloride, AR grade : Merck

17. Calcium Chloride, AR grade : Merck
 18. Aluminium sulfate hydrate, AR grade : Merck

2.2 Equipments

1. 5-Necked round bottom reactor, 2 L capacity with condenser
2. Brookfield viscometer : Brookfield Engineering, Model LVT
3. pH meter : Metler, Model Delta 340
4. Oven : Binder, Model FD115/E2
5. Bird Type Applicator (casting bar) : Sheen
6. Particle size : Malvern 4700
7. GPC : Water 150-CV
8. Minimum Film Forming Temperature Bar : Rhopoint Instrumentation
9. Stirrer : Sheen
10. Gloss meter : BYK Gardner
11. Scanning Electron Microscopy : JEOL, Model JSM-6400

2.3 Procedure

2.3.1 Pre-emulsion testing

The efficiency of each surfactant was tested by observation of the monomer pre-emulsion formation. Each surfactant as an emulsifier was dissolved in deionized water in a 1 L beaker. The mixture of monomers was then added into the gently stirred solution. The recipe used for pre-emulsion testing was shown in Table 2.1. After 10 minutes of stirring, the stirring speed was gradually increased to 1000 rpm and stirred for another 10 minutes.

The emulsion was placed in a 100 mL cylinder for observation of the phase separation of the emulsion at 3 hours.

Table 2.1 Recipe used for pre-emulsion testing.

Ingredients	% by weight
Deionized water	26.22 %
Emulsifier (100% active ingredient)	0.22 %
Methyl methacrylate	46.33 %
Butyl acrylate	26.13 %
Methacrylic acid	1.10 %
Total	100.00 %

2.3.2 Polymerization process

The latex was prepared by emulsion polymerization. Six different dosages of reagents were separately prepared (Table 2.2). Five dosages (A-E) were used during the polymerization step (Part A) and the sixth dosage (F) was used in the post polymerization step (Part B). Dosage A was the monomer pre-emulsion prepared in section 2.3.1. Dosage B was an aqueous solution of the initiator, ammonium persulfate, prepared in a 50 mL beaker. Dosage C prepared in a 2 L five-necked reactor, equipped with a condenser, a thermocouple thermometer, a mechanical stirrer, a stopper and a feeding line (Figure 2.1). Dosage C was stirred at 70 rpm until all the solid was dissolved and then heated to 80 °C. Dosage B was added into the reactor when the reactor temperature had leveled off at 80 – 83 °C. After the addition of dosage B for 5 minutes, Dosage A was slowly fed into the reactor over 3 hours while keeping the reaction temperature in the range of 80 – 88 °C. The stirring speed during the feeding was increased stepwise as following; 70 rpm in the first hour, 100 rpm in the second hour, 120 rpm in the third hour and 150 rpm after completion of the feeding of dosage A. The reaction temperature was controlled in the range of 80 – 88 °C for an additional 30 minutes before dosage D, a solution of *tert*-butyl hydroperoxide, was added. After another 30 minutes, dosage E, a solution of sodium formaldehyde

sulfoxylate-B, was added into the reactor. The polymerization was continued for an additional 90 minutes at 80 – 88 °C. The resulting latex obtained was allowed to cool to room temperature and filtered through a 200 mesh filter into 1 L beaker.

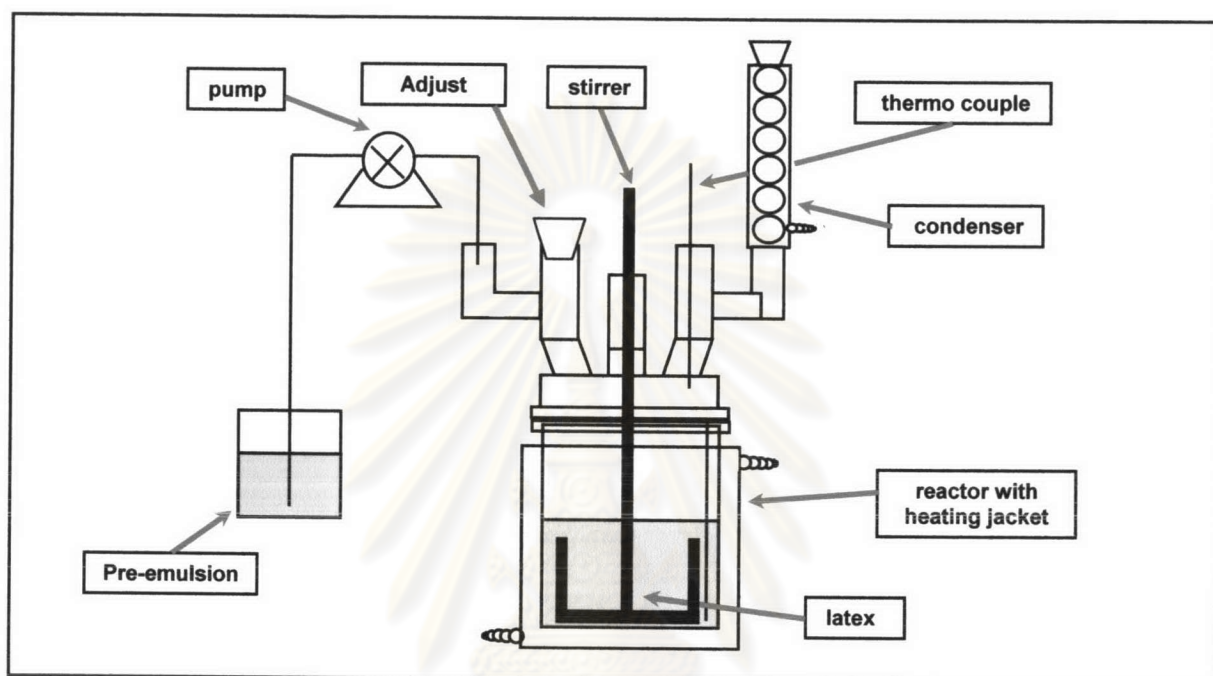


Figure 2.1 Apparatus for emulsion copolymerization of methyl methacrylate, butyl acrylate and methacrylic acid monomers.

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Table 2.2 Dosages of reagents used in the polymerization

Part A: Polymerization step			
Dosage	Description	Ingredients	% by weight
A	Monomer pre-emulsion	Deionized water	17.62
		Emulsifier (100% solid)	0.15
		Methyl methacrylate	31.16
		Butyl acrylate	17.57
		Methacrylic acid	0.74
B	Initiator	Deionized water	1.06
		Ammonium persulfate	0.28
C	Medium	Deionized water	29.09
		Emulsifier (100% solid)	0.20
		Sodium carbonate	0.16
D	Initiator	Tertiary butyl hydroperoxide	0.06
E	Initiator	Deionized water	0.12
		Sodium formaldehyde sulfoxylate-B	0.04
TOTAL			100.00
Part B: Post polymerization			
Dosage	Description	Ingredients	% by weight
F	Additive	Mixture of part A	95.84
		Butyl cellosolve	1.24
		Texanol	0.49
		Formaldehyde solution	0.16
		Ammonia solution 26%	0.30
		Deionized water	1.97
TOTAL			100.00

Dosage F prepared in a separated 50 mL beaker, a solution of butyl cellosolve, texanol, formaldehyde and ammonia, was continuously fed into the latex within 1 hour while stirring at 600 rpm. The pH value of the latex was adjusted to 8–9 with 26% ammonia solution. The polymerization procedure described above was summarized schematically in Figure 2.2.



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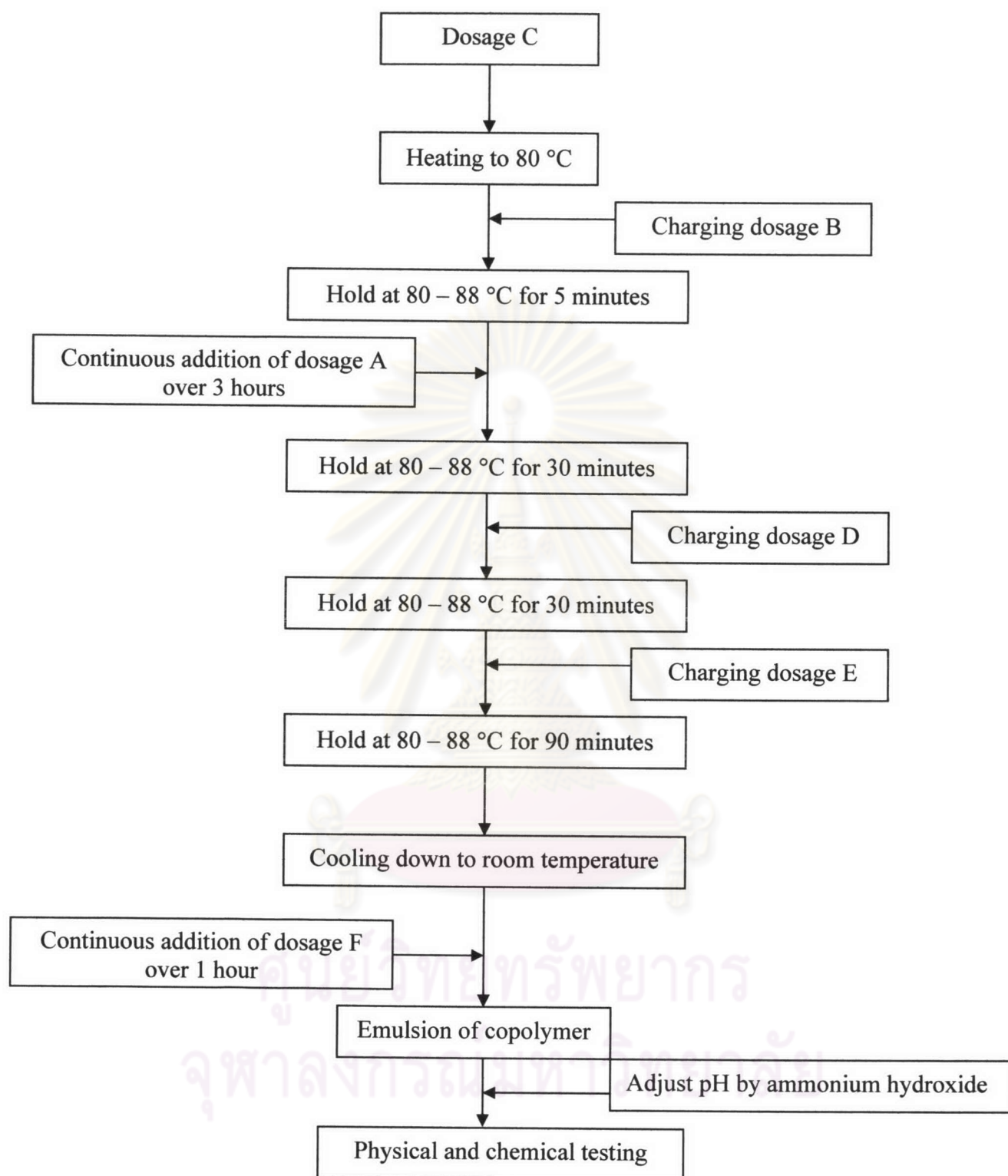


Figure 2.2 The overall schematic experimental procedure

2.3.3 Physical and chemical testing

2.3.3.1 Film appearance (SM-TM007) [24]

A latex sample was spread with a 100 μm thickness casting bar over a glass slide (10 cm \times 15 cm) and allowed to dry at room temperature until it formed a thin film (\sim 50 μm thickness). The film was evaluated for transparency by visual observation.

2.3.3.2 Viscosity measurement (ASTM D2196-99)

The viscosity of the latex was measured by Brookfield viscometer LVT. A latex sample (600 g) was filled in a 600 mL low-shaped beaker and thermostated at 25 $^{\circ}\text{C}$. A spindle (number 1) was placed into the latex. During the spindle was settled into the latex, it had to be hold diagonal and slightly twisted, to avoid formation of bubbles below the stirring disk. The measurement took place at 30 rpm. The viscometer was allowed to run until the pointer was stabilized. The viscosity (η) was calculated from the reading value (S) taken from the viscometer display according to the following equation.

$$\eta = 2S$$

η = viscosity in cP

2 = factor of spindle no. 1 at 30 rpm

S = value taken from the viscometer display

2.3.3.3 Measurement of nonvolatile content (ASTM D2369)

A latex sample (0.7 g) was filled into a dry pre-weighed aluminium foil pan. After baking at 140 $^{\circ}\text{C}$ for 90 minutes, the weight of the dry latex was determined and % nonvolatile weight was calculated. The latex was measured for 4 times for each sample and the average nonvolatile content was calculated.

2.3.3.4 Determination of particle size

The particle size within the latex was determined from Malvern instrument series 4700 at the following conditions: air cooled argon ion laser, $\lambda = 488 \text{ nm}$; dispersing

medium = deionized water filtered by 0.21 micron membrane filter; scattering angle = 90°; temperature = 30 °C; viscosity of dispersing medium = 0.798 cP; refractive index of dispersing medium = 1.330. The cell was filled with about 15 mL of deionized water, then a solution of diluted latex was dropped into the cell. The filled-cell was immersed in the water chamber with thermostat at 25°C for at least 5 minutes before starting the measurement. After 5 minutes, latex particle size was measured by the instrument. The counting number of the particles per second was around 100 – 200 counts. The measurement was repeated three times for each latex.

2.3.3.5 Determination of molecular weight

The molecular weight of copolymer within the latex was determined by Gel Permeation Chromatography, Waters 150-CV at the following conditions: eluent = tetrahydrofuran; flow rate = 1.0 ml/min; injection volume = 100 µl; temperature = 30 °C; column set = PL gel 10 µm mixed B 2 columns (MW resolving range = 500 – 10,000,000); standard = polystyrene (MW 5,460 – 1,290,000); detector: refractive index detector. A latex sample was spread with a 100 µm thickness casting bar over a glass slide (10 cm × 15 cm) and allowed to dry at room temperature until it formed a thin film (~ 50 µm thickness). The latex film (10 mg) was dissolved in tetrahydrofuran (5 mL) and kept overnight in refrigerator. The solution was filtered by 0.45 micron membrane and injected to the GPC instrument.

2.3.3.6 Stability testing [23]

The latex (200 g) was charged into a 250 mL bottle. The bottle was tightly closed and placed in an incubator at 50 °C for 1 week. The appearance of the latex was recorded and the degree of coagulum was determined by visual observation.

2.3.3.7 Determination of the water and alkaline resistance of polymer films

Two polymer films with a thickness of 100 µm were prepared with a casting bar on two glass-slides (10 cm × 15 cm). The wet films were cured at 35°C for 30 minutes and allowed to dry at room temperature for 48 hours, on a horizontal surface. After drying, one glass-slide was immersed in tap water at the half-height and another slide in 3% NaOH

solution. The film appearance was observed after 3, 6, 24, and 48 hours and rated as follows:

0 = clear film, unchanged	3 = turbid, still transparent film
1 = partly, light turbid film	4 = partly white film
2 = light, turbid film	5 = totally white film

2.3.3.8 Freeze – thaw stability

A latex sample (300 g) was filled into a 500 mL bottle. The bottle was tightly closed and placed in the chamber maintained at $-10\text{ }^{\circ}\text{C}$. The bottles were kept in the chamber for 17 hours and allowed to stand for 7 hours undisturbed at room temperature (1 cycle). The process was repeated for 5 cycles. After 5 cycles, the latex was rated for any evidence of settling, gelation, coagulation as follows:

10 = none	4 = moderate
8 = very slight	2 = considerable
6 = slight	0 = completely failure

2.3.3.9 Determination of electrolyte stability of polymer latex [23]

A latex sample (10 mL) was mixed with 10 mL of the following salt solutions:

1% NaCl sol.	1% CaCl_2 sol.	1% $\text{Al}_2(\text{SO}_4)_3$ sol.
10% NaCl sol.	10% CaCl_2 sol.	10% $\text{Al}_2(\text{SO}_4)_3$ sol

The latex was visually evaluated as follows:

- no coagulum latex is stable, remark if increased viscosity was noted
- coagulum formation latex is not stable

2.3.3.10 Determination of minimum film forming temperature (MFFT) (SK-TM002) [24]

The suitable temperature program of MFFT instrument was selected (the MFFT of latex must stayed in the temperature range of this temperature program). A latex sample was applied by using $75\text{ }\mu\text{m}$ cube applicator from the warm end to the cold end. All latex samples should be applied within 10 minutes, and then closed with the cover. After 1 hour, the temperature where the film had coalesced over 90% of the track width was recorded as

the MFFT of the latex. The measurement of the MFFT of each latex was repeated for three times.

2.3.3.11 Determination of gloss of dry film

A latex sample was spread with a 100 μm thickness casting bar over a glass slide (10 cm \times 15 cm). The wet films were cured at 35°C for 30 minutes and allowed to dry at room temperature for 24 hours, on a horizontal surface. The gloss of the dry film was measured by a gloss meter, measuring the light passing through the aperture which was projected from the light source inside the instrument.

2.3.3.12 Scanning Electron Microscopy (SEM) of latex particle size

The scanning Electron Microscopy (SEM) was used to confirm the latex particle size. Latex samples for SEM were dropped on a SEM stub and tested specimens were coated with gold. The measurement was operated at 15 KV.



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