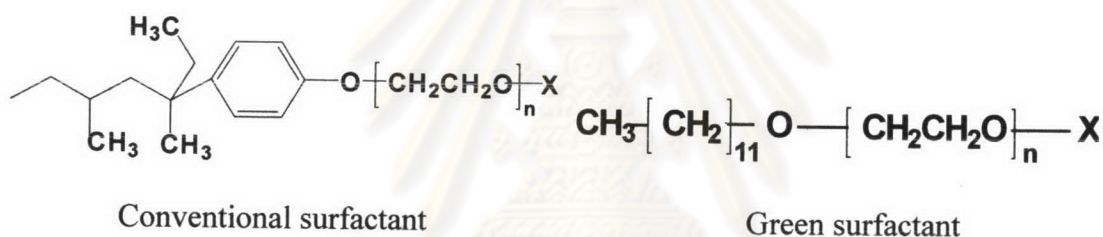


CHAPTER III

RESULTS AND DISCUSSION

In this work, 20 surfactants were evaluated for their effectiveness to be used in the preparation of the latex from emulsion copolymerization of methyl methacrylate, butyl acrylate and methacrylic acid monomers. The surfactants are classified into 4 groups, 1. nonylphenol ethoxylate (NPE), 2. fatty alcohol ethoxylate (FAE), 3. nonylphenol ethoxylate sulfate (NPES), and 4. fatty alcohol ethoxylate sulfate (FAES), representing the conventional nonionic, green nonionic, conventional anionic (Na salt) and green anionic (Na salt) surfactants respectively. In each group, the number of ethoxyl groups (EO number, n) belonging to the ethylene glycol part of the surfactants was varied (Figure 3.1).



Nonionic: nonylphenol ethoxylate
 $X = H$
 $n = 4, 6, 9, 15, 30$ and 40

Nonionic: fatty alcohol ethoxylate
 $X = H$
 $n = 7, 10, 15, 30$ and 40

Anionic: nonylphenol ethoxylate sulfate
 $X = SO_3$
 $n = 4, 10$ and 40

Anionic: fatty alcohol ethoxylate sulfate
 $X = SO_3$
 $n = 4, 12, 30$ and 40

Figure 3.1 The structures of the surfactants used

3.1 Pre-emulsion

The first step in this work is to identify the ability and stability of the surfactants to disperse the monomers in the emulsion formation before initiating the polymerization. All 20 surfactants were tested by mixing the monomers with a tested surfactant in water and observed the stability of the emulsion for 3 hours. If there was a separation observed within 3 hours the stability was recorded as “fail” otherwise recorded as “pass”.

There was no significant difference between the nonylphenol and fatty alcohol surfactants in their emulsifying ability (Table 3.1). The anionic surfactants however seemed to have better emulsifying ability than the nonionic surfactants. While all the anionic surfactants could provide stable monomer pre-emulsion even at concentration as low as 0.22% w/w, the nonionic surfactants with shorter ethoxyl chain required higher concentration used. The emulsifying ability of the nonionic surfactants increased with the increasing length of the ethoxyl chain. With ethoxyl chain longer than 30, the nonionic surfactants could provide stable emulsion comparable to their anionic counterparts even at low surfactant concentration.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.1 The stability of pre-emulsion formed with the tested surfactants

EO number (n)	%by weight	Stability of pre-emulsion			
		NPE	NPES	FAE	FAES
4	0.22	Fail	Pass	-	Pass
	0.44	Fail	Pass	-	Pass
	0.66	Pass	Pass	-	Pass
	0.88	Pass	Pass	-	Pass
	1.32	Pass	Pass	-	Pass
6	0.22	Fail	-	-	-
	0.44	Fail	-	-	-
	0.66	Pass	-	-	-
	0.88	Pass	-	-	-
	1.32	Pass	-	-	-
7	0.22	-	-	Fail	-
	0.44	-	-	Fail	-
	0.66	-	-	Pass	-
	0.88	-	-	Pass	-
	1.32	-	-	Pass	-
9	0.22	Fail	-	-	-
	0.44	Fail	-	-	-
	0.66	Pass	-	-	-
	0.88	Pass	-	-	-
	1.32	Pass	-	-	-
10	0.22	-	Pass	Fail	-
	0.44	-	Pass	Fail	-
	0.66	-	Pass	Pass	-
	0.88	-	Pass	Pass	-
	1.32	-	Pass	Pass	-
12	0.22	-	-	-	Pass
	0.44	-	-	-	Pass
	0.66	-	-	-	Pass
	0.88	-	-	-	Pass
	1.32	-	-	-	Pass
15	0.22	Fail	-	Fail	-
	0.44	Pass	-	Pass	-
	0.66	Pass	-	Pass	-
	0.88	Pass	-	Pass	-
	1.32	Pass	-	Pass	-
30	0.22	Pass	-	Pass	Pass
	0.44	Pass	-	Pass	Pass
	0.66	Pass	-	Pass	Pass
	0.88	Pass	-	Pass	Pass
	1.32	Pass	-	Pass	Pass
40	0.22	Pass	Pass	Pass	Pass
	0.44	Pass	Pass	Pass	Pass
	0.66	Pass	Pass	Pass	Pass
	0.88	Pass	Pass	Pass	Pass
	1.32	Pass	Pass	Pass	Pass

3.2 Use of nonionic surfactants in emulsion polymerization

The first property to be studied for the effects of the type of surfactants on the emulsion polymerization was the appearance of the resulting latex and its stability upon storage. The polymerization recipe is shown in Table 2.2 while the polymerization process is shown in Figure 2.2. The polymerization was also performed using the conventional anionic surfactant with EO number of 4, (no 1 Table 3.2) currently used in the plant for comparison. The ethoxyl chain length of the surfactants and the amount of the surfactants were varied. The stability of the latex was tested by observation of the copolymer emulsion at room temperature after a storage period of 1 month (Table 3.2).

Table 3.2 Appearance of the latices using nonionic surfactants.

No.	Surfactant in pre-emulsion		Surfactant in reactor		Latex product		Film appearance
	type	%	type	%	After the reaction	After 1 month	
1	NPES-4	0.15	NPES-4	0.20	milky	milky	clear
2	NPE-7	0.15	NPE-7	0.20	solid	-	-
3	NPE-7	0.45	-	-	milky	precipitated	-
4	NPE-7	0.45	NPE-7	0.60	gel	-	-
5	NPE-40	0.15	NPE-40	0.20	milky	precipitated	-
6	NPE-40	0.45	NPE-40	0.60	gel	-	-
7	NPES-4	0.45	NPE-40	0.60	milky	milky	opaque
8	NPES-4	0.45	NPE-40	1.20	gel	-	-

Initiator concentration = 0.28% w/w

The attempt to use only nonionic surfactant in emulsion polymerization was not successful. No homogeneous and stable latex was obtained from the polymerization using a pure nonionic surfactant (no. 2-6 Table 3.2) even when the nonionic surfactant with the longest ethoxyl chain ($n = 40$) was used at the concentration three times higher than the current dosage used for the anionic surfactant. At high concentration of nonionic surfactant,

the polymerization led to the formation of latex gel (no.4, 6 and 8). The gelation started after 1 hour of the continuous feeding of the monomer pre-emulsion. The results suggested that nonionic surfactants were not suitable for emulsion polymerization of the studied monomers. Later experiments were thus focused only on the anionic surfactants.

3.3 Use of green surfactants in emulsion polymerization

One of the main objectives of this research work was to study the possibility in replacing the conventional surfactants used in the industrial plant (Rhodia PPMC Thailand) with the green surfactants. A group of green surfactants of nonionic and anionic surfactants was selected to be used in the emulsion polymerization. The polymerization was also performed by using the conventional anionic surfactant with EO number of 4 (no 1 Table 3.3) currently used in the plant for comparison. The concentrations of each selected surfactant used in the pre-emulsion and in the reactor were either at the same concentrations applied in the plant or at the minimum concentration required for the emulsion formation of the monomers. The stability of the latex was tested by observation of the copolymer emulsion at room temperature upon storage for 1 month. The stable emulsion was recorded as “pass” and the settled emulsion was recorded as “fail”.

Both nonylphenol and fatty alcohol anionic surfactants with EO number of 40 did not provide clear latex film and stable emulsion upon storage for 1 month while the shorter ethoxyl chain did. There was no significant difference between the conventional and green surfactants in their ability to stabilize the latex particles. The green fatty alcohol surfactants may be used in place of the conventional nonylphenol surfactants.

Table 3.3 Appearance of the latices using anionic surfactants.

Surfactant	%Surfactant in reactor	Latex appearance	Film	Latex stability
NPES-4	0.10	Milky	clear	pass
	0.20	milky	clear	pass
	0.30	milky	clear	pass
	0.60	milky	clear	pass
	0.90	milky	clear	pass
NPES-10	0.10	milky	clear	pass
	0.20	milky	clear	pass
	0.30	milky	clear	pass
NPES-40	0.10	milky	turbid	fail
	0.20	milky	turbid	fail
	0.30	milky	turbid	fail
FAES-4	0.10	milky	clear	pass
	0.20	milky	clear	pass
	0.30	milky	clear	pass
	0.60	milky	clear	pass
	0.90	milky	clear	pass
FAES-12	0.20	milky	clear	pass
FAES-30	0.20	milky	clear	pass
FAES-40	0.20	milky	turbid	fail

Initiator concentration = 0.28% w/w,

%active ingredient of surfactant in pre-emulsion = 0.15% w/w

3.4 Properties of latices obtained from emulsion polymerization using anionic conventional and green surfactants

3.4.1 Latex viscosity

3.4.1.1 Effect of the degree of ethoxylation of the surfactants

Anionic surfactants, both nonyl phenol ethoxylate sulfate and fatty alcohol ethoxylate sulfate, with various EO numbers were used in the same quantity and condition to synthesize the copolymer latices by emulsion polymerization. All latices obtained from the polymerization were adjusted to obtain 49 – 51% non-volatile content (%NV) and pH 8 – 9 according to the factory specification. The viscosity of the copolymer emulsion was determined by Brookfield viscometer model LVT at 25°C. The latex viscosity was rather independent on the degree of ethoxylation of the surfactants with EO number ranging from 4 to 30 (Table 3.4). At EO number being 40, the viscosity of the latex however sharply decreased due to coagulation during polymerization leading to the latex with lower %NV than the specification. The results suggested that, in the preparation of latices from the emulsion copolymerization of methyl methacrylate and butyl acrylate using nonyl phenol ethoxylate sulfate and fatty alcohol ethoxylate sulfate anionic surfactants, the degree of ethoxylation of the surfactants used should be lower than 40.

Table 3.4 Effect of EO number of surfactant on latex viscosity

Surfactant	Viscosity (cP)
NPES-4	80
NPES-10	90
NPES-40	14*
FAES-4	90
FAES-12	92
FAES-30	97
FAES-40	14*

*: partially coagulate during polymerization

3.4.1.2 Effect of surfactant concentration

Four anionic surfactants, three from nonyl phenol ethoxylate sulfate series (EO number = 4, 10 and 40) and one from fatty ethoxylate sulfate series (EO number = 4), were used in this experiment. The concentration of each anionic surfactant in the total formulation was varied from 0.25% to 1.05% w/w. The viscosity of the latex increased with the concentration especially obvious for fatty alcohol ethoxylate sulfate surfactant (Figure 3.2). As the concentration of monomers being constant, the increase of the surfactant concentration would increase the number of the micelles containing monomer droplets with reducing sizes in the emulsion as well as the number and sizes of the particles in the resulting latex. The increasing number of the particles of the latex usually results in rising viscosity.

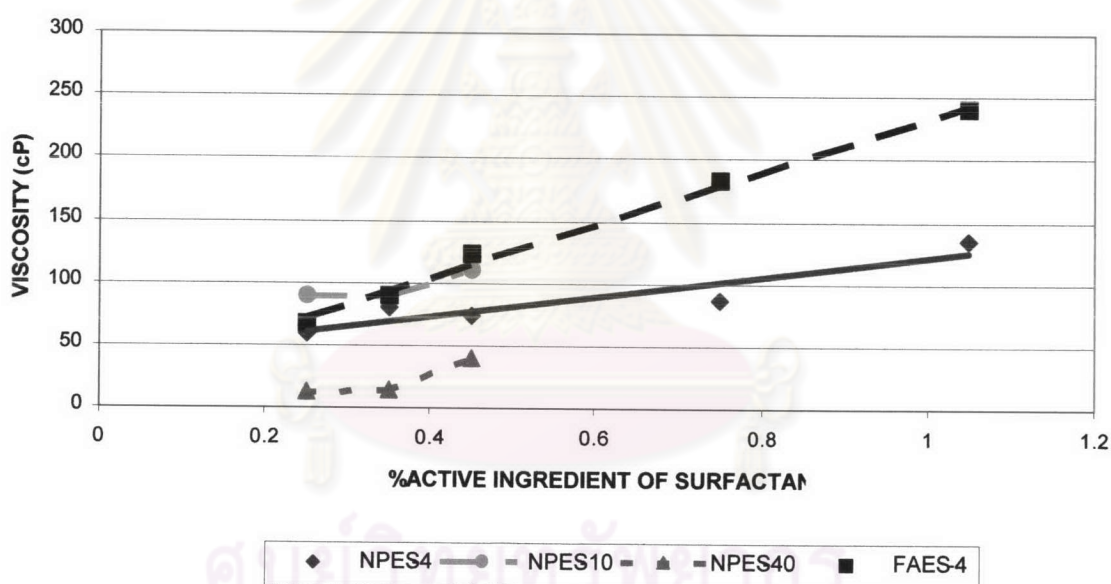


Figure 3.2 Viscosity of the resulting latex versus %surfactant in emulsion polymerization

3.4.2 Particle size

3.4.2.1 Effect of degree of ethoxylation of the surfactants

The particle sizes of the latex obtained from the emulsion polymerization using anionic surfactants with various degree of ethoxylation, at 0.35% w/w, were measured by laser-light scattering technique. Each sample was measured in triplicates to give the average particle size. The use of higher degree of ethoxylation surfactants gave relatively larger

average particle sizes of the latex. As the molecular weight of the surfactant increased with the EO number, the molarity of the surfactant with higher EO number was lower. With lower molarity, the surfactant molecules usually form fewer but larger micelles surrounding the monomer droplets. The particle size of the latex obtained from the polymerization using fatty alcohol ethoxylate sulfate with EO number of 40 was so large (710.3 nm) that it settle upon storage and it was not included in Figure 3.4.

3.4.2.2 Effect of surfactant concentration

The relationships between the latex particle sizes and the concentration of the surfactants used were studied. The latex particle sizes seemed to be reduced with the increasing concentration of the surfactants. The result supports the hypothesis in section 3.4.2.1 proposed for the increase of the latex viscosity with the increasing concentration of the surfactants used. In the presence of high concentration of the surfactants, the monomers from monomer droplets tend to form new latex particles rather than going into the old monomer swollen particles because there are enough of surfactant molecules to stabilize the new latex particle in the system. On the other hand, in the system with lower surfactant concentration, the monomers tend to go into the old monomer swollen particles and the polymerization occurs inside those particles to form even larger sizes of the latex particles. Another factor usually influencing the particle sizes of the latex is the stirring speed. The high stirring speed will give the small latex particle size. In this experiment, the stirring speed in all the polymerization was cautiously controlled within fixed speed at any period of reaction.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

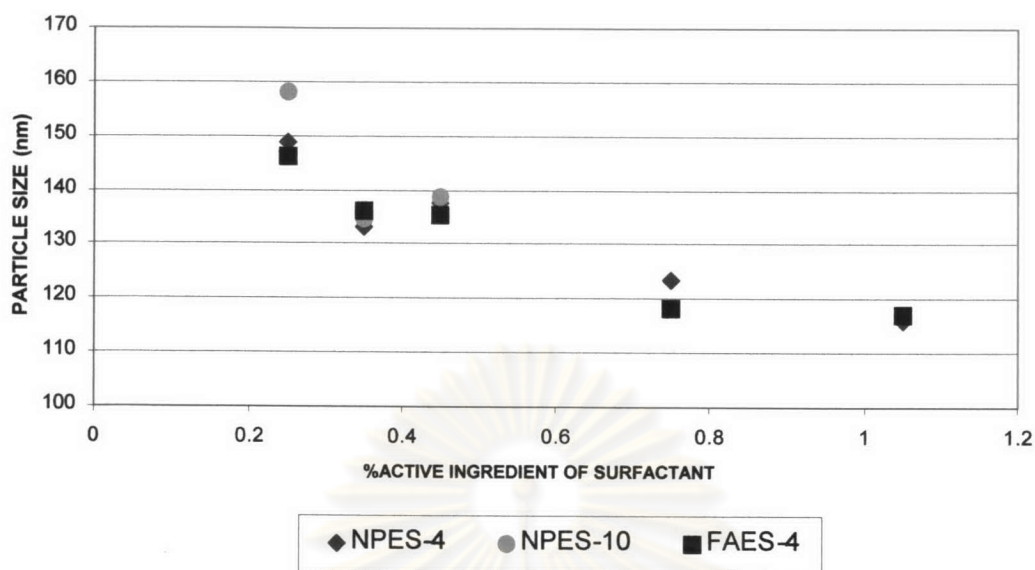


Figure 3.3 Average particle size of the resulting latex versus %surfactant in polymerization mixture

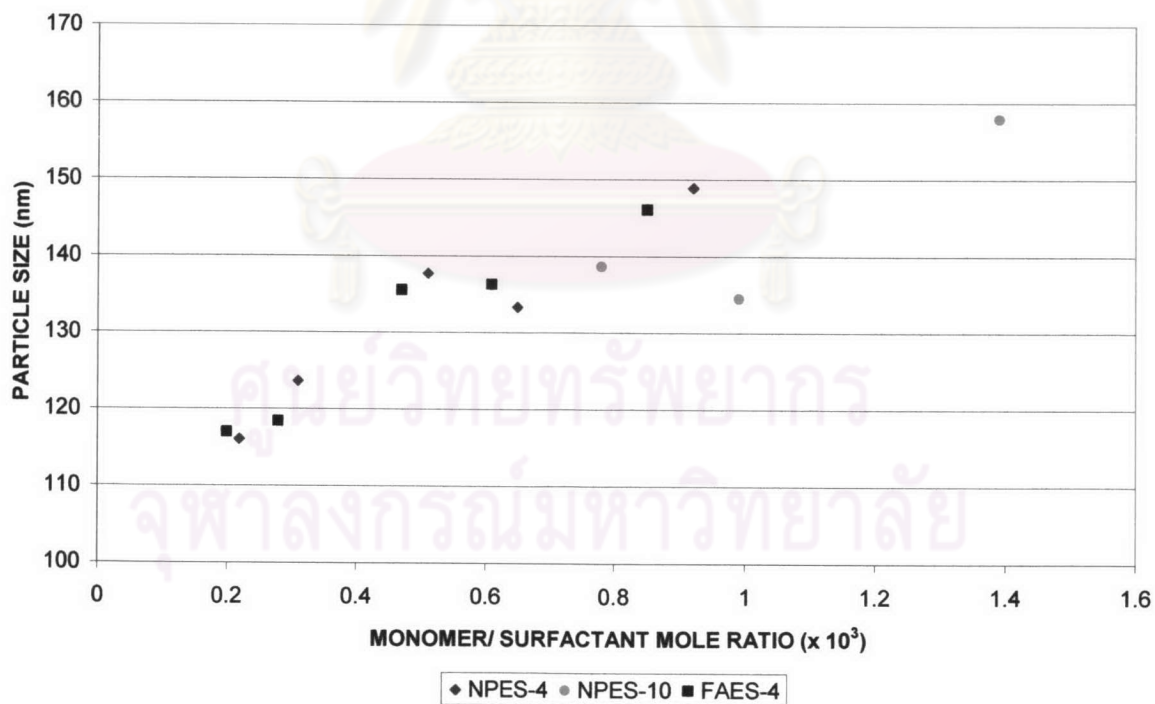


Figure 3.4 Average particle size of the resulting latex versus monomer/ surfactant mole ratio ($\times 10^3$)

The latex viscosity is usually reduced with the increasing particle size [20]. Interestingly, the plot between the viscosity versus the particle size of the latex obtained from the polymerization using various surfactants in this work also showed this trend (Figure 3.5) despite the fact that the latex contained different type of surfactants at different concentrations. This indicated that the latex particle size is one of the most important factors governing the viscosity of the latex with the same nonvolatile content. The smaller particle size means the higher particle density and so the viscosity of the emulsion.

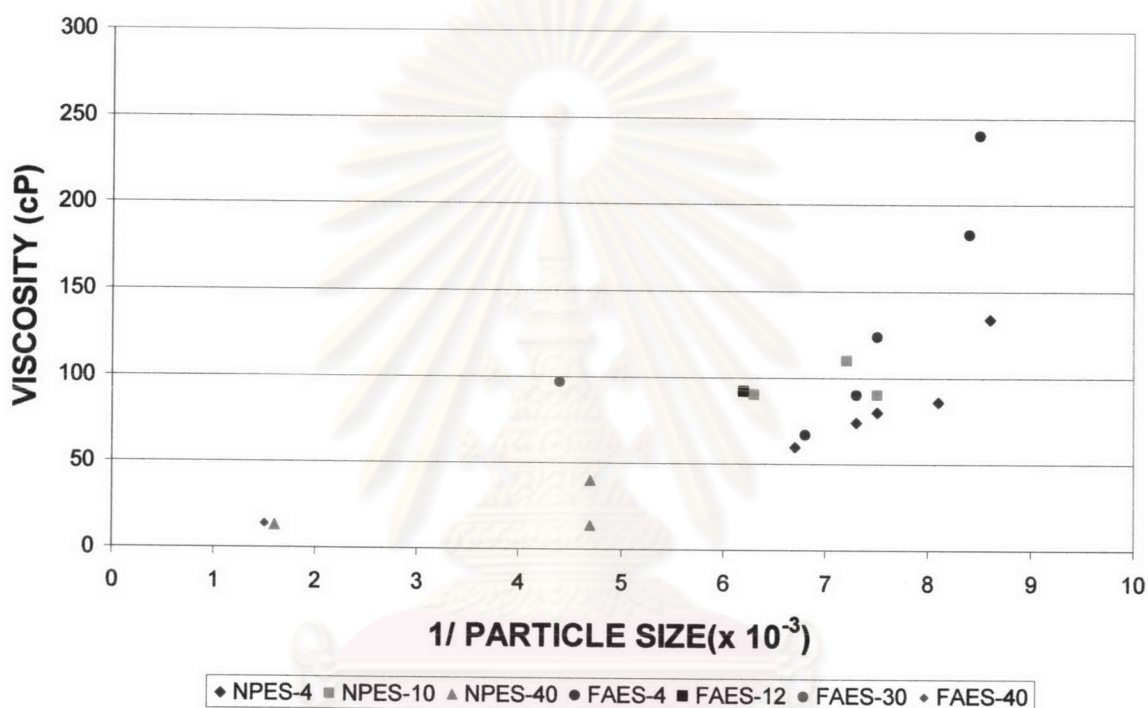


Figure 3.5 The relationship between average latex particle size and latex viscosity

3.4.3 Molecular weight

The molecular weight of the latices were determined with GPC. Poor solubility of the latex posed some difficulty in obtaining solution suitable for the GPC analysis. The molecular weights of some latex samples showed significant degree of deviation when being repeated (Table 3.5). The molecular weights of these latices were in the same range of $4 \times 10^4 - 1 \times 10^5$ for M_n and $2 \times 10^5 - 5 \times 10^5$ for M_w with polydispersities ranging between 4 and 8. These figures of the molecular weights are slightly lower than the values reported for emulsion polymerization of methyl methacrylate-2-ethyl hexyl acrylate copolymer ($\sim M_n$ was 2×10^5 and $M_w \sim 1 \times 10^6$) [21].

It was hard to draw any relationships between the molecular weights of the polymers and the types of surfactants used in these experiments as the magnitude of deviation between the repetitive analysis was about the same as the entire range of the molecular weight spreading due to different types of surfactants used. Besides the molecular weight determined here may not represent the whole samples of the latices due to their poor solubility.

Table 3.5 The average molecular weights of the latices obtained from the polymerization with various surfactants

Surfactant	Concentration used (%)	Molecular weight		PDI
		Mn (10^4)	Mw (10^5)	
NPES-4	0.25	7.63	3.71	4.86
NPES-4 (repeated)	0.25	10.24	5.63	5.50
NPES-4	0.35	4.25	1.96	4.62
	0.45	5.39	3.12	5.79
	0.75	7.91	4.68	5.92
	1.05	6.82	4.01	5.88
NPES-4 (repeated)	1.05	4.56	1.90	4.16
NPES-10	0.25	6.46	4.38	6.78
	0.35	6.64	3.24	4.88
	0.45	6.25	3.25	5.20
NPES-40	0.25	6.71	3.09	4.61
	0.35	4.55	2.44	5.37
	0.45	7.79	4.07	5.23
FAES-4	0.25	4.41	2.21	5.01
FAES-4 (repeated)	0.25	3.03	1.91	6.31
FAES-4	0.35	7.00	3.39	4.85
	0.45	4.03	2.02	5.01
	0.75	3.38	1.65	4.88
	1.05	2.88	1.93	6.69
FAES-4 (repeated)	1.05	3.80	2.24	5.90
FAES-12	0.35	9.12	4.21	4.62
FAES-30	0.35	6.59	5.04	7.65
FAES-40	0.35	9.97	5.23	5.24

3.4.4 Latex stability

Two samples from each latex were studied for their stability at 60°C and at room temperature. It was found that almost all latices have good storage stability in both conditions except for the latices possessing average particle size larger than 200 nm (Table 3.6). The surfactants which provide small latex particle size lead to good stability of the latex. From the latex stability point of view, fatty alcohol ethoxylate sulfate with EO number of 30 and 40 and nonylphenol ethoxylate sulfate with EO number of 40 are not suitable for preparation of the latex from this copolymer emulsion.

Table 3.6 The effect of type and surfactant concentration on latex stability

Group	Surfactant		Particle size (nm)	Appearance	
	Concentration used (%)			Storage at 60°C	Storage at room temperature (3 months)
NPES-4	0.25		148.9	milky	milky
	0.35		133.3	milky	milky
	0.45		137.7	milky	milky
	0.75		123.6	milky	milky
	1.05		116.1	milky	milky
NPES-10	0.25		157.9	milky	milky
	0.35		134.5	milky	milky
	0.45		138.6	milky	milky
NPES-40	0.25		611.8	precipitated	precipitated
	0.35		211.7	milky	precipitated
	0.45		213.4	milky	precipitated
FAES-4	0.25		146.0	milky	milky
	0.35		136.3	milky	milky
	0.45		133.5	milky	milky
	0.75		118.4	milky	milky
	1.05		117.0	milky	milky
FAES-12	0.35		150.0	milky	milky
FAES-30	0.35		228.6	milky	precipitated
FAES-40	0.35		710.3	precipitated	precipitated

3.4.5 Water / alkaline stability

The water and alkaline resistance of the latex films were evaluated by visual observation giving the scale ranging from 0-5. The score 0 indicated a transparent film and the score 5 indicated a totally white film. When the surfactants were used at the concentration 0.25 – 0.45% (no. 1-3, 6-13, and 16 Table 3.7), all dry films from latex had the same water resistance. When the dosage of surfactant used was increased to 0.75% w/w or higher (no. 4, 5, 14 and 15), the water resistance of dry film slightly improved. This result might be resulted from the particle size of the latices. The smaller latex particle size may allow tighter and denser film formation than the bigger latex particle size does. Also note that the surfactants, which gave large latex particles (no. 17 and 18), produced the film with poorer water resistance.

Table 3.7 Water resistance of dry film

No.	Surfactant		Particle size (nm)	Film appearance				
	Group	Concentration used (%)		initial	3 hrs	6 hrs	24 hrs	48 hrs
1.	NPES-4	0.25	148.9	0	2	2	3	3
2.		0.35	133.3	0	2	2	3	3
3.		0.45	137.7	0	2	2	3	3
4.		0.75	123.6	0	2	2	2	2
5.		1.05	116.1	0	2	2	2	2
6.	NPES-10	0.25	157.9	0	2	2	3	3
7.		0.35	134.5	0	2	2	3	3
8.		0.45	138.6	0	2	2	3	3
9.	NPES-40	0.35	211.7	0	2	2	3	3
10.		0.45	213.4	0	2	2	3	3
11.	FAES-4	0.25	146.0	0	2	2	3	3
12.		0.35	136.3	0	2	2	3	3
13.		0.45	133.5	0	2	2	3	3
14.		0.75	118.4	0	2	2	2	2
15.		1.05	117.0	0	2	2	2	2
16.	FAES-12	0.35	150.0	0	2	2	3	3
17.	FAES-30	0.35	228.6	0	2	3	3	4
18.	FAES-40	0.35	710.3	2	2	3	3	4

With various surfactant concentrations from 0.25 – 1.05% w/w, all dry films from latex had the same alkaline resistance except for the dry films from the latex obtained from the polymerization using nonylphenol ethoxylate sulfate with EO number of 40 and fatty alcohol ethoxylate sulfate with EO number 30 and 40 were apparently poorer than the others. These results can also be rationalized in term of the latex particle size similar to the results observed in the water resistance experiment.

Table 3.8 Alkaline resistance of dry film

No.	Surfactant		Particle size (nm)	Film appearance				
	Group	Concentration used (%)		initial	3 hrs	6 hrs	24 hrs	48 hrs
1.	NPES-4	0.25	148.9	0	0	0	0	2
2.		0.35	133.3	0	0	0	0	2
3.		0.45	137.7	0	0	0	0	2
4.		0.75	123.6	0	0	0	0	2
5.		1.05	116.1	0	0	0	0	2
6.	NPES-10	0.25	157.9	0	0	0	0	2
7.		0.35	134.5	0	0	0	0	2
8.		0.45	138.6	0	0	0	0	2
9.	NPES-40	0.35	211.7	0	2	2	2	2
10.		0.45	213.4	0	2	2	2	2
11.	FAES-4	0.25	146.0	0	0	0	0	2
12.		0.35	136.3	0	0	0	0	2
13.		0.45	133.5	0	0	0	0	2
14.		0.75	118.4	0	0	0	0	2
15.		1.05	117.0	0	0	0	0	2
16.	FAES-12	0.35	150.0	0	0	0	0	2
17.	FAES-30	0.35	228.6	0	2	2	2	2
18.	FAES-40	0.35	710.3	2	3	3	3	3

3.4.6 Electrolyte stability

The electrolyte stability of the latices was evaluated by visual observation. The results were recorded as (-) for stable and (+) for coagulated latex. When the surfactants were used at the concentration higher than 0.75% for nonylphenol ethoxylate sulfate (no. 4 and 5 Table 3.9) and higher than 0.45% for fatty alcohol ethoxylate sulfate (no. 13-15 Table 3.9), the electrolyte stability of the latices was decreased. The latex with bigger particle size tended to have a little better electrolyte stability than the latex with smaller particle size. As the electrolytes destabilize the latex particle by salting out the surfactant, smaller latex particles can quickly move themselves close to each other to reduce their unfavorable surface interaction with water. The type and concentration of cation would effect to the stability of the latex. The increasing in the electrolyte solution concentration and the higher charge of the cations makes the latex coagulates easier. All latices were thus stable in the 1% NaCl solution than in CaCl_2 and $\text{Al}_2(\text{SO}_4)_3$ solution respectively. Some of the latices were not stable in 10%NaCl solution and most of them were not stable in CaCl_2 and $\text{Al}_2(\text{SO}_4)_3$ solution excepted for the latex with unusually large particle size

Table 3.9 Electrolyte stability of the latex

No	Surfactant		Particle size (nm)	Latex appearance					
	Group	Concentration used (%)		NaCl		CaCl ₂		Al ₂ (SO ₄) ₃	
				1%	10%	1%	10%	1%	10%
1.	NPES-4	0.25	148.9	-	-	-	+	+	+
2.		0.35	133.3	-	-	-	+	+	+
3.		0.45	137.7	-	-	-	+	+	+
4.		0.75	123.6	-	+	-	+	+	+
5.		1.05	116.1	-	+	-	+	+	+
6.	NPES-10	0.25	157.9	-	-	-	+	+	+
7.		0.35	134.5	-	-	-	+	+	+
8.		0.45	138.6	-	-	-	+	+	+
9.	NPES-40	0.35	211.7	-	-	-	+	+	+
10.		0.45	213.4	-	-	-	+	+	+
11.	FAES-4	0.25	146.0	-	-	+	+	+	+
12.		0.35	136.3	-	-	+	+	+	+
13.		0.45	133.5	-	+	+	+	+	+
14.		0.75	118.4	-	+	+	+	+	+
15.		1.05	117.0	-	+	+	+	+	+
16.	FAES-12	0.35	150.0	-	-	-	+	+	+
17.	FAES-30	0.35	228.6	-	-	-	-	+	+
18.	FAES-40	0.35	710.3	-	-	-	-	-	+

- ; no coagulum + ; coagulum

3.4.7 Minimum Film Forming Temperature (MFFT)

The Minimum Film Forming Temperature (MFFT) is one of the most important properties of the latex. It represents how difficult for the latex to form a film. The higher MFFT values, the more difficult to form the film, and normally the latex with low MFFT is preferred. The MFFT was measured by the MFFT bar. There was no significant difference between the latices obtained from the polymerization using conventional and green anionic

surfactants. The degree of ethoxylation and the surfactant concentration did not effect to the MFFT of the resulting latex as all MFFT were observed in the same range (24.6 – 27.0 °C) (Table 3.10).

Table 3.10 Minimum film forming temperature (MFFT) of the latex.

Surfactant	Concentration used (%)	Average MFFT (°C)
NPES-4	0.25	25.0
	0.35	25.8
	0.45	24.6
	0.75	24.4
	1.05	24.2
NPES-10	0.25	25.8
	0.35	25.8
	0.45	25.6
NPES-40	0.25	26.5
	0.35	26.9
	0.45	26.7
FAES-4	0.25	26.1
	0.35	26.9
	0.45	26.8
	0.75	26.3
	1.05	26.0
FAES-12	0.35	26.2
FAES-30	0.35	27.0
FAES-40	0.35	27.0

3.4.8 Freeze-thaw stability

The effect of surfactant on freeze-thaw stability of the latex was studied by observing the appearance of the latex after it was freezed at -10 °C for 17 hours and thawed at room temperature for 7 hours. This one cycle took 24 hours and a latex was tested for 5

cycles. The stability was recorded as “stable” for the latex which did not form any noticeable changes, otherwise recorded as “unstable”. The concentration of the surfactants has more obvious effect to the freeze-thaw stability of the latex than the surfactant type (Table 3.11). The suitable concentration of the surfactants was in the range of 0.35 – 0.45% to provide latices with good freeze-thaw stability.

Table 3.11 Freeze-thaw stability of the latex

Surfactant		Latex appearance				
Group	Concentration used (%)	Number of cycle				
		1	2	3	4	5
NPES-4	0.25	Unstable	-	-	-	-
	0.35	Stable	Stable	Stable	Stable	Stable
	0.45	Stable	Stable	Stable	Stable	Stable
	0.75	Stable	Stable	Stable	Stable	Coagulate
	1.05	Stable	Stable	Stable	Unstable	-
NPES-10	0.25	Unstable	-	-	-	-
	0.35	Stable	Stable	Stable	Stable	Stable
	0.45	Stable	Stable	Stable	Stable	Stable
NPES-40	0.35	Stable	Stable	Stable	Stable	Stable
	0.45	Stable	Stable	Stable	Stable	Stable
FAES-4	0.25	Stable	Stable	Stable	Stable	Stable
	0.35	Stable	Stable	Stable	Stable	Stable
	0.45	Stable	Stable	Stable	Stable	Stable
	0.75	Unstable	-	-	-	-
	1.05	Unstable	-	-	-	-
FAES-12	0.35	Stable	Stable	Stable	Stable	Stable
FAES-30	0.35	Stable	Stable	Stable	Stable	Stable
FAES-40	0.35	Stable	Stable	Stable	Stable	Stable

3.4.9 Gloss value of dry film

A high quality latex normally gives a film with high gloss value. The gloss value of dry film was measured by gloss meter ten times for each film. The use of either nonylphenol or fatty alcohol surfactants gave relatively the same gloss value (Table 3.12). All the surfactants gave acceptable values of gloss (over 100) excepted for the surfactant with EO number of 40. The concentration of the surfactants also did not affect the gloss of the latex film.

Table 3.12 Gloss value of the dry film

Surfactant	Concentration used (%)	Gloss value
NPES-4	0.25	110.0
	0.35	112.8
	0.45	115.0
	0.75	110.4
	1.05	114.3
NPES-10	0.25	111.1
	0.35	116.4
	0.45	113.2
NPES-40	0.25	88.8
	0.35	90.7
	0.45	91.9
FAES-4	0.25	114.6
	0.35	110.4
	0.45	116.6
	0.75	115.1
	1.05	109.4
FAES-12	0.35	109.1
FAES-30	0.35	111.8
FAES-40	0.35	86.6

3.5 Emulsion polymerization using mixed surfactants

There are reports claiming that nonionic surfactants can improve freeze-thaw and electrolyte stability of the latex [12, 13], so the polymerization was also conducted by using mixed anionic and nonionic surfactants. The mixing ratios (in reactor) between the nonionic fatty alcohol ethoxylate with EO number of 40 and the anionic fatty alcohol ethoxylate sulfate with EO number of 4 surfactant were 1 : 1 and 3 : 1 w/w. The polymerization recipe is shown in Table 2.2 and the polymerization process is shown in Figure 2.2.

3.5.1 Latex viscosity, Particle size and Molecular weight

Mixed surfactants with two ratios, 1:1 and 3:1 w/w in the reactor or 1:2.50 and 1:1.33 w/w in total formulation, between nonionic and anionic fatty alcohol ethoxylate surfactant, were used in the same quantity (0.35% w/w) and condition to synthesize the copolymer latices by emulsion polymerization. All latices obtained from the polymerization were adjusted to have 49 – 51% non-volatile content (%NV) and pH 8 – 9 according to the factory specification. The viscosity of the copolymer emulsion was determined by Brookfield viscometer model LVT at 25 °C. The particle sizes of the latices were measured by laser-light scattering technique. Each sample was measured in triplicates to give the average particle size. The molecular weight of the latices were determined with GPC. There was no significant different in viscosity and molecular weight of the latex from anionic green surfactant and mixed green surfactant (Table 3.13). But the use of higher ratio of nonionic surfactant gave relatively larger average particle sizes of the latex agreeing with the literature work [20].

Table 3.13 The viscosity, particle size and molecular weight of the latex obtained from mixed surfactants

Surfactant	Viscosity (cP)	Particle size (nm)	Molecular weight	
			M_n (10^4)	M_w (10^5)
FAES-EO4	67	136.3	7.00	3.39
FAE-40 : FAES-4 (1: 2.50)	72	153.3	4.01	1.75
FAE-40 : FAES-4 (1: 1.33)	76	187.5	7.06	4.10

3.5.2 Latex stability

Two samples from each latex were studied for their stability at 60°C and at room temperature. It was found that all latices have good storage stability in both conditions (Table 3.14).

Table 3.14 Stability of the latex obtained from mixed surfactant

Surfactant	Appearance	
	Storage at 60°C	Storage at room temperature (3 month)
FAES-EO4	Milky	Milky
FAE-40 : FAES-4 (1: 2.50)	Milky	Milky
FAE-40 : FAES-4 (1: 1.33)	Milky	Milky

3.5.3 Water / alkaline resistance of the dry film

The water and alkaline resistance of the latex films were evaluated by visual observation. There was no significant difference between anionic and mixed surfactants (Table 3.15 and Table 3.16).

Table 3.15 Water resistance of the dry film from mixed surfactant

Surfactant	Film appearance				
	initial	3 hrs	6 hrs	24 hrs	48 hrs
FAES-EO4	0	2	2	3	3
FAE-40 : FAES-4 (1: 2.50)	0	2	2	3	3
FAE-40 : FAES-4 (1: 1.33)	0	2	2	3	3

Table 3.16 Alkaline resistance of the dry film from mixed surfactant

Surfactant	Film appearance				
	initial	3 hrs	6 hrs	24 hrs	48 hrs
FAES-EO4	0	0	0	0	2
FAE-40 : FAES-4 (1: 2.50)	0	0	0	0	2
FAE-40 : FAES-4 (1: 1.33)	0	0	0	0	2

3.5.4 Electrolyte stability

The latices obtained from mixed surfactants had a little poorer electrolyte stability in CaCl_2 than the latex obtained from anionic surfactant. The blending of nonionic surfactant in anionic surfactant cannot improve the electrolyte stability of the latices which disagreed with the literature work [12, 13].

Table 3.17 Electrolyte stability of the latex from mixed surfactant

No.	Group of surfactant	Latex appearance					
		NaCl		CaCl ₂		Al ₂ (SO ₄) ₃	
		1%	10%	1%	10%	1%	10%
1.	anionic	-	-	-	+	+	+
2.	FAE-40 : FAES-4 (1: 2.50)	-	-	+	+	+	+
3.	FAE-40 : FAES-4 (1: 1.33)	-	-	+	+	+	+

- ; no coagulum

+ ; coagulum

3.5.5 Minimum film forming temperature (MFFT) and Gloss value of dry film

The MFFT of all latices and the gloss value of the dry films were in the same range (Table 3.18).

Table 3.18 Minimum Film Forming Temperature of the latex and gloss value of the dry film obtained from mixed surfactant .

Surfactant	MFFT of the latex (°C)	Gloss value of the dry film
FAES-EO4	26.9	110.4
FAE-40 : FAES-4 (1: 2.50)	26.4	114.7
FAE-40 : FAES-4 (1: 1.33)	26.1	111.6

3.5.6 Freeze-thaw stability

There was no different in freeze-thaw stability of the latex obtained from anionic and mixed surfactant.

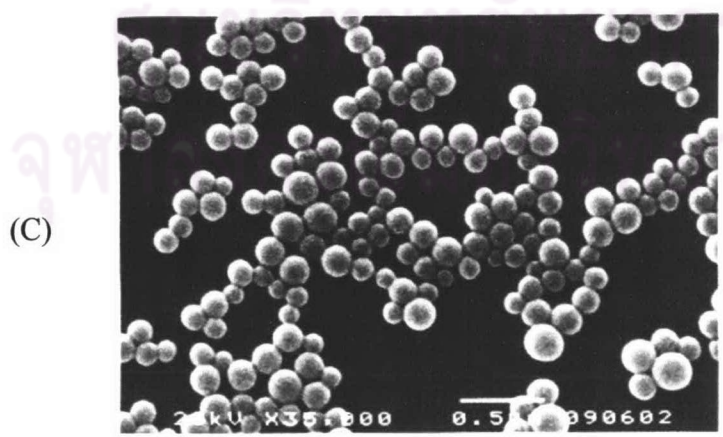
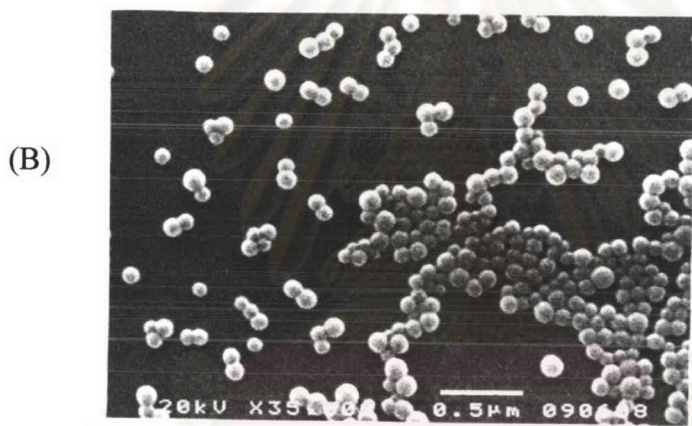
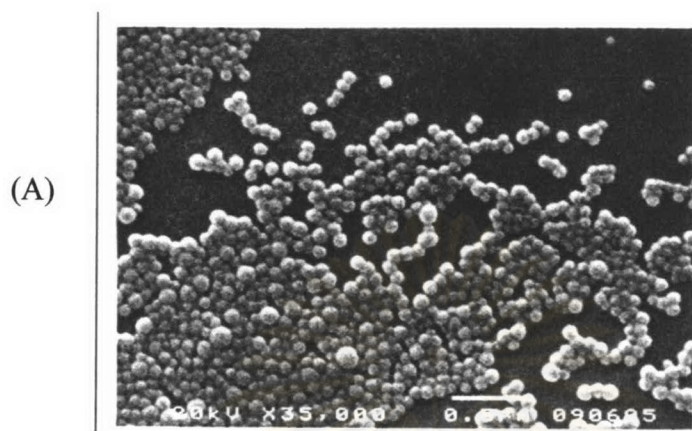
Table 3.19 Freeze-thaw stability of the latex obtained from mixed surfactant

Surfactant	Latex appearance				
	Number of cycle				
	1	2	3	4	5
FAES-EO4	Stable	Stable	Stable	Stable	Stable
FAE-40 : FAES-4 (1: 2.50)	Stable	Stable	Stable	Stable	Stable
FAE-40 : FAES-4 (1: 1.33)	Stable	Stable	Stable	Stable	Stable

3.6 Scanning Electron Microscopy (SEM) of the latex

The scanning electron microscopy of the latex was conducted to confirm the particle size of the latex obtained from the light scattering technique. The tested latices

showed that the particle sizes observed from the electron micrographs were comparable to the average particle sizes obtained from the light scattering technique (Figure 3.6).



(D)

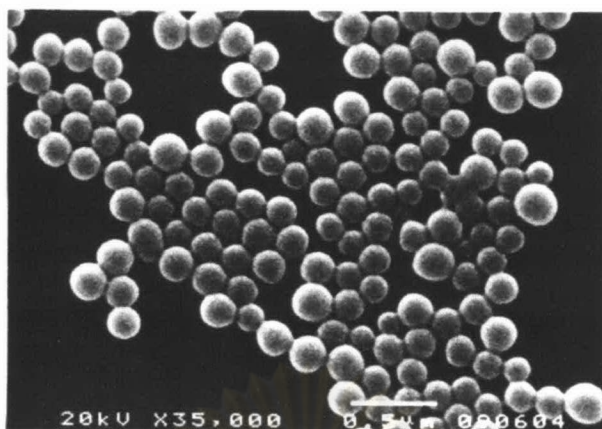


Figure 3.6 Scanning Electron Microscopy (SEM) of the latex particles obtained from the emulsion polymerization using

- (A), 1.05% of NPES-4 (116.1nm)
- (B), 0.35% of NPES-4 (133.3 nm)
- (C), 0.35% of 3 : 1 w/w ratio of FAE-40 : FAES-4 (187.5 nm)
- (D), 0.35% of NPES-40 (211.7 nm)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย