

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Poly HIPE Preparations

4.1.1 PolyHIPE Reference

The polyHIPE reference was prepared at first without the amine compounds in the system. It was used as a reference for guideline to synthesize the polyHIPE with amines. To find a suitable condition for the emulsion systems, it is needed to vary the amount of surfactant, because surfactants play an important role for stabilization of the emulsion. As shown in Table 3.1 and in recipes 1-6, the surfactant ratio (SpanR80: Triton X-100) is varied from 1.33 – 4 and SEM results are shown in Figure 4.1.

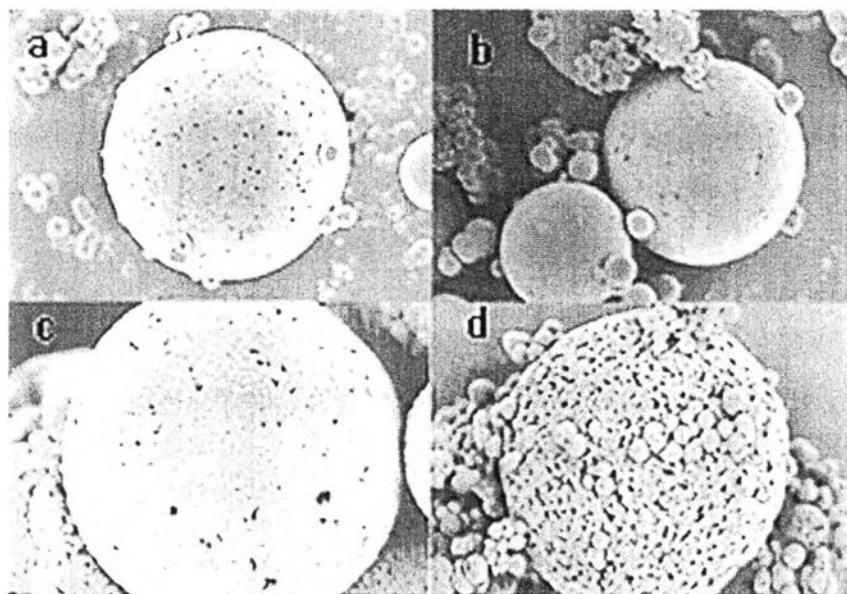


Figure 4.1 SEM micrographs of polyHIPE reference with magnification of x20K, surfactant ratio of (a) 1.0, (b) 1.18, (c) 1.33, (d) 1.54.

The polyHIPE were spherical shape with void and fracture appearance. The morphology shows surface roughness formed by small spheres agglomeration (Figure 4.2) for water in oil in water (w/o/w) emulsion where water

droplet was stabilized by the oil soluble surfactant inside the oil droplet of the emulsion (w/o) of the oil droplet in water (w/o/w) emulsion. At a low concentration of oil soluble surfactant, but still higher than the critical micelle concentration (cmc) of SpanR80, the simple spherical reverse micelle was formed. The reverse micelle sphere trapped water inside, after the emulsion polymerization and the water was removed, the void was consequently formed. At high oil soluble surfactant concentration, spherical micelles could probably be transformed to different reverse micellar shapes, such as lamellar and bilayer etc., which resulted in different structure of polyHIPE (Zhou et al., 2007).

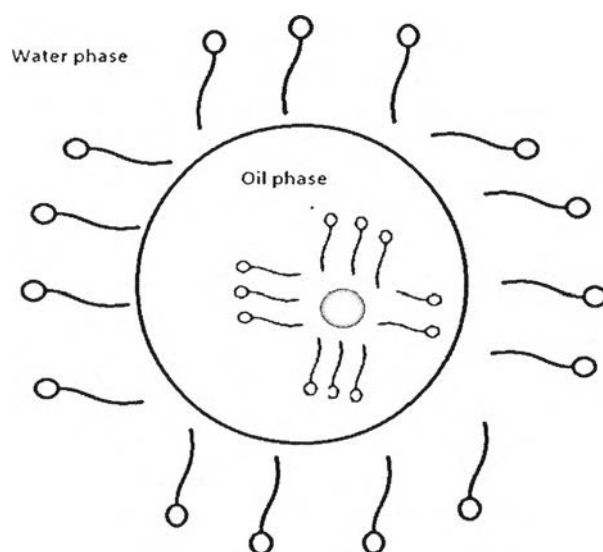


Figure 4.2 Void and fracture formation from the effect of oil soluble surfactant.

When the surfactant ratio was 2, SEM is shown in Figure 4.3. The appearance of the polyHIPE is similar to the previous result, but there are many big open cavities on the surface of the spheres.

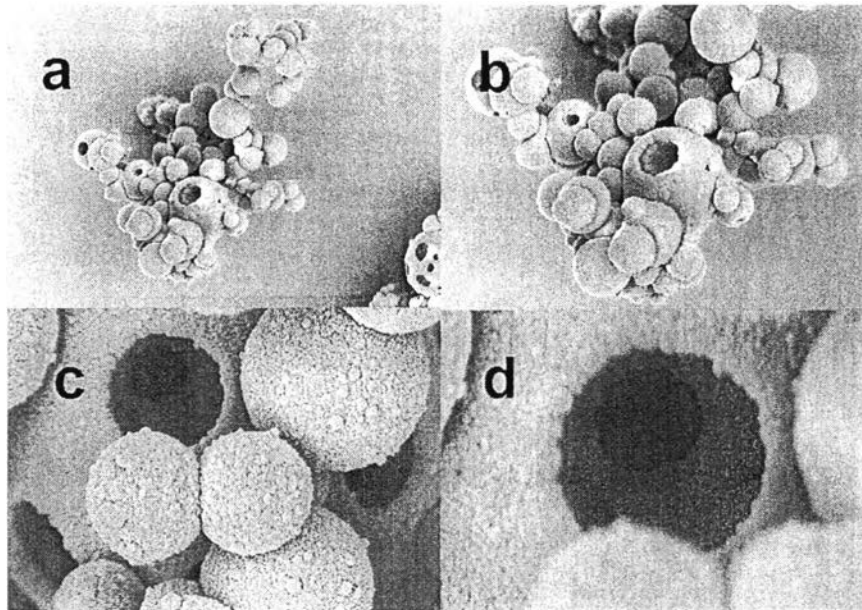


Figure 4.3 SEM micrographs of polyHIPE with magnifications of (a) x10K (b) x20K (c) x50K (d) x100K, with SpanR80:Triton X-100 = 2.

Figure 4.4 shows morphology of the polyHIPE at the surfactant ratio of 4. There is no spherical shape like that of the two previous conditions. It agglomerates in each other and does not have void or fracture because the emulsion system is not stable. Therefore, the condition with the surfactant ratio of 1.33 and 1/18 were arbitrarily chosen for further study.

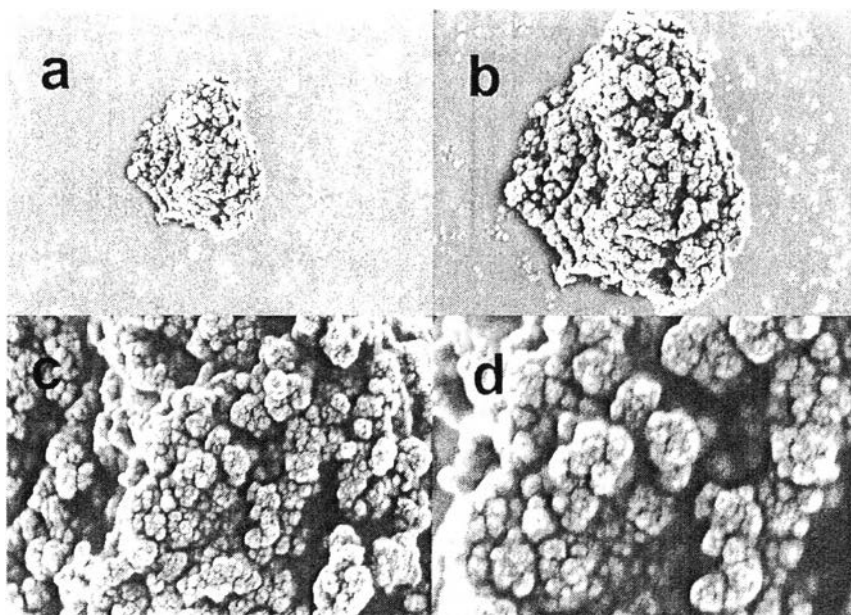


Figure 4.4 SEM micrographs of polyHIPE with magnifications of (a) x10K (b) x50K (c) 50K (d) 100K of polyHIPE with SpanR80:Triton X-100 = 4.

4.1.2 PolyHIPE with Amines

4.1.2.1 *PolyHIPE with Hexylamine*

Hexylamine, which is medium chain length (6 carbon atoms), can be easily dissolved in oil phase where the polymerization reaction can occur. It was initially reacted with VBC at the mole ratio of VBC to hexylamine of 1:1.07 at 65 °C for 15 min and then the product VB-hexylamine was mixed with other ingredients in the oil phase. To confirm the reaction between VBC and hexylamine, the product of VBC-hexylamine from the reaction was characterized by FTIR as shown in Figure 4.5.

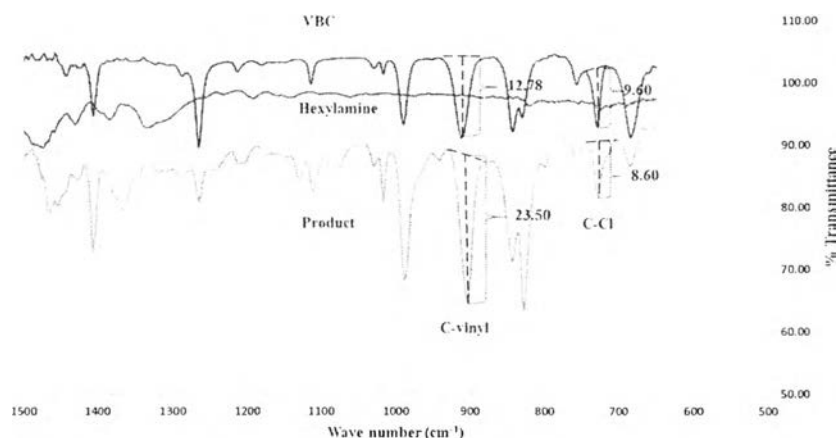


Figure 4.5 FTIR spectra of hexylamine, VBC, and VBC-hexylamine product.

Figure 4.5 shows the spectral comparison of VBC, hexylamine and the product of VB-hexylamine. The spectrum of VBC shows characteristic bending vibration of C-vinyl at 911 cm^{-1} and C-Cl stretching vibration at 729 cm^{-1} . The peak intensity ratio of C-Cl to C-vinyl is always constant at 0.75. In the presence of hexylamine, the reaction takes place between the amine group of hexylamine and C-chloride group of VBC (reaction number 4.1) which decreases the peak intensity of C-chloride and thus, causes the peak ratio to decrease to 0.37. The conversion of the reaction (percent yield of VB-hexylamine formation) of 51.27 % can be calculated from the change in the intensity ratio as shown in Table 4.1. The product contains secondary amine in the VB-hexylamine structure; however, the vibration frequency at 750 cm^{-1} of secondary amine wagging vibration observed in the FTIR spectrum. When VB-hexylamine was incorporated in the emulsion polymerization and in the polyHIPE-hexylamine formation, the FTIR spectrum was obtained but the percent of hexylamine in the polyHIPE structure could not be calculated by the measurement of the peak ratio of C-vinyl to C-Cl as it was done for VBC because the vinyl group was disappeared in the polymerization. Thus, percent of hexylamine in the polyHIPE-hexylamine was determined by a CHN analyzer for percent of nitrogen. The % nitrogen value was then converted to the amount of amine in polyHIPE-hexylamine. This analysis was also used for polyHIPE-1,3-diminopropane.

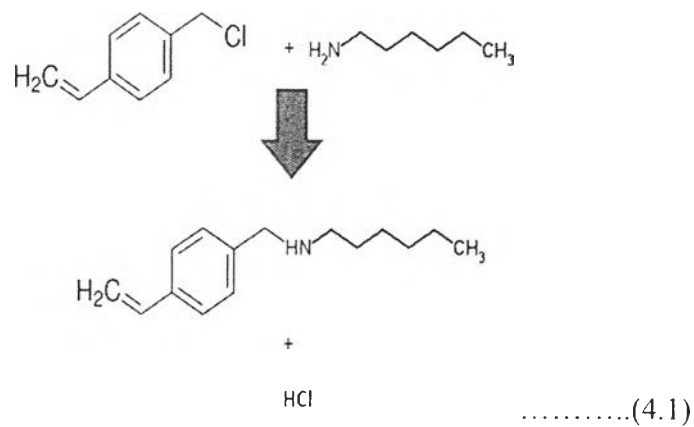


Table 4.1 Peak ratio calculation

Spectra	Wave number C-Cl / C=CH ₂	Peak ratio	% Conversion
VBC	729/911	$\frac{9.60}{12.78} = 0.75$	$\frac{0.75 - 0.37}{0.751} \times 100 = 51.27\%$
VB- hexylamine	728/903	$\frac{8.60}{23.50} = 0.37$	

After characterization by FTIR, all of condition of polyHIPE with hexylamine were synthesized and checked for the morphology by SEM as shown in Figure 4.6.

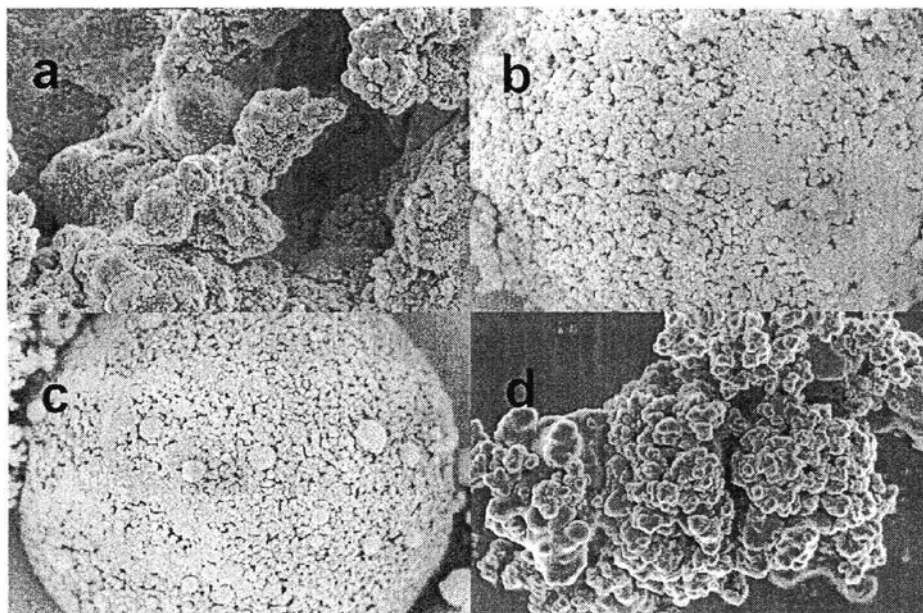


Figure 4.6 SEM micrographs of polyHIPE with hexylamine with magnification $\times 20K$. surfactant ratio of (a) 1.2, (b) 1.33, (c) 1.50, (d) 1.71.

For surfactant ratios of 1.33 and 1.50, the morphology of polyHIPE with hexylamine shown in Figure 4.6 (b) and (c) look like the sphere which occurred in polyHIPE reference, where void and fracture appears on the surface. On the other hand, conditions which surfactant ratios of 1.2 and 1.71, the void and fracture does not appear.

4.1.2.2 PolyHIPE with 1,3-Diaminopropane

Another type of amine is 1,3-diaminopropane, which there are two amino groups attached at both end of the structure, leading to more opportunity for adsorbing CO_2 than hexylamine in the polyHIPE. Like hexylamine, the mole ratio of this reaction used was 1 mole of VBC to 1.07 mole of 1,3-diaminopropane. To confirm the reaction between VBC and 1,3-diaminopropane, the product was characterized by FTIR as shown in Figure 4.7. The peak intensity ratio of C-Cl to $C=CH_2$ vibration was calculated (Table 4.2) and showed a decrease in the value indicating the reaction between VBC and 1,3-diaminopropane. The percent conversion was 56.00 %.

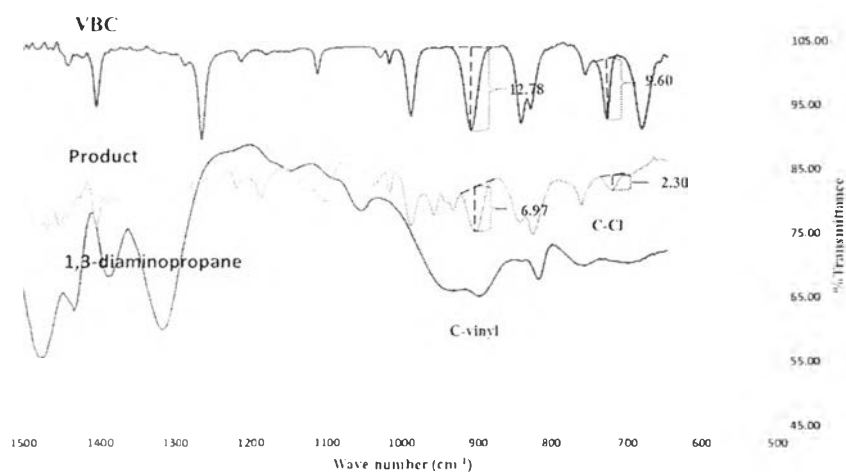


Figure 4.7 FTIR spectra of 1,3-diaminopropane, VBC and VBC-1,3-diaminopropane product.

Table 4.2 Peak ratio calculation

Spectra	Wave number C-Cl, C=CH ₂	Peak ratio	% Conversion
VBC	911/729	$\frac{9.6}{12.78} = 0.75$	$\frac{0.75 - 0.33}{0.75} \times 100 = 56.00\%$
VB-1,3-diaminopropane	903/728	$\frac{2.3}{6.97} = 0.33$	

The SEM micrographs of polyHIPE with 1,3-diaminopropane are presented in Figure 4.8 and Figure 4.9. The surfactant ratios of 0.72, 0.76, 0.87 and 0.94 do not form the polyHIPE sphere, but the agglomeration of ununiformed shape of polyHIPE. For the surfactant ratio of 0.81, the morphology showed many incomplete spheres and also void and fracture on the surface. The morphology of polyHIPE with 1,3-diaminopropane is different from that of polyHIPE-hexylamine because 1,3-diaminopropane contains amino groups on both ends which allows higher possibility for VBC to react and also more polar structure than hexylamine. The polar-polar repulsion may prevent sphere formation.

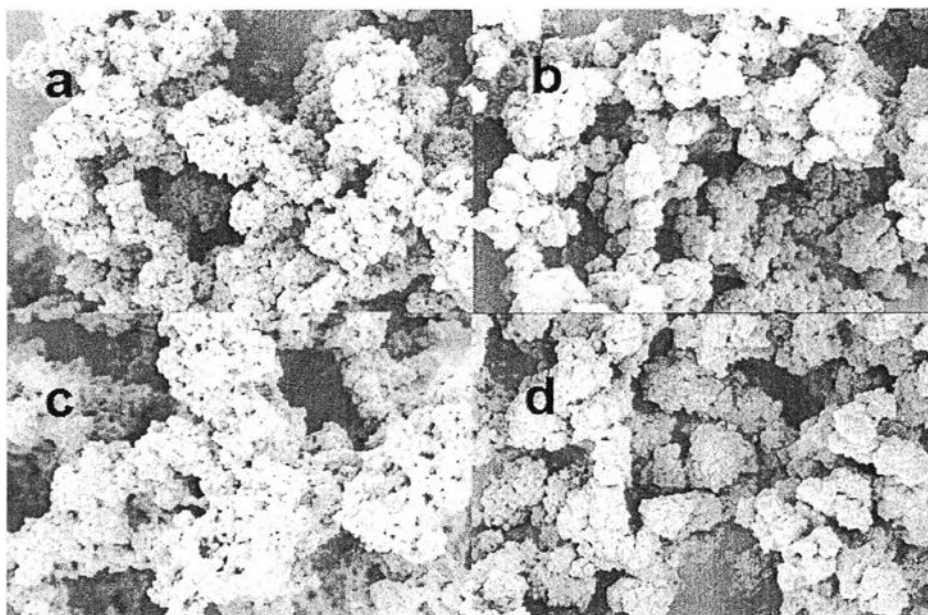


Figure 4.8 SEM micrographs of polyHIPE with 1,3-diaminopropane with magnification x20K, surfactant ratio of (a) 0.72, (b) 0.76, (c) 0.87, (d) 0.94.

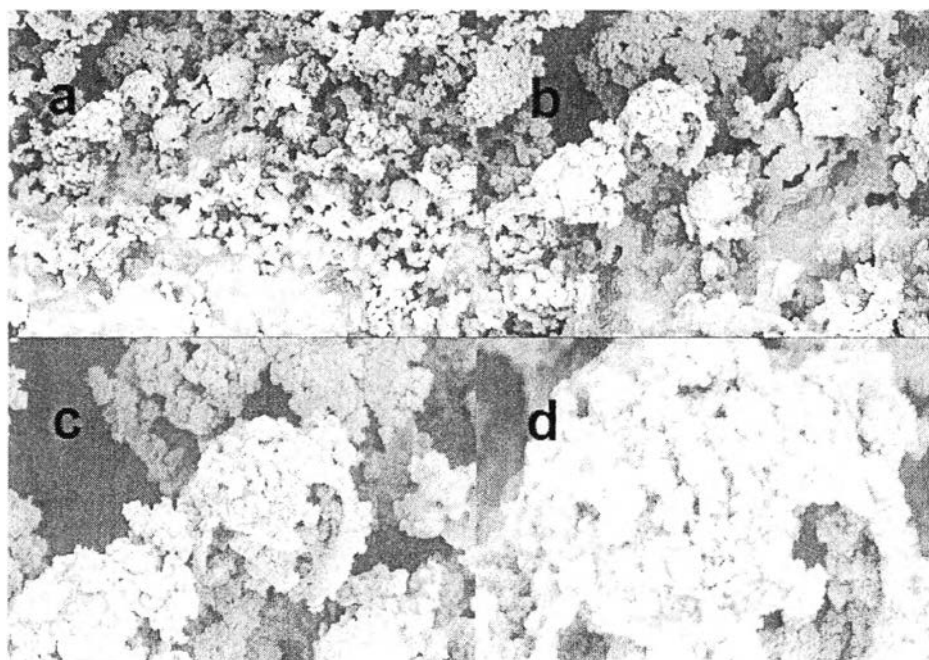


Figure 4.9 SEM micrographs of polyHIPE with 1,3-diaminopropane with surfactant ratio of 0.81, magnification (a) x5K, (b) x10K, (c) x20K, (d) x50K.

4.2 Characterization of PolyHIPE

4.2.1 Surface Area of PolyHIPE

The surface areas of polyHIPE reference and the polyHIPE with amine were measured by surface area analyzer (Autosorb-IMP) under N₂ ambient condition and the result are shown in Table 4.3.

Table 4.3 Surface area of polyHIPE

Recipe	Surfactant ratio	Surface area (m ² /g)	Remark
1	1.00	91.28	PolyHIPE reference
2	1.18	106.00	
3	1.33	102.60	
4	1.54	89.38	
5	2.00	65.16	
7	1.20	17.77	PolyHIPE-hexylamine
8	1.33	38.75	
9	1.50	88.05	
10	1.71	25.63	
11	0.72	2.93	PolyHIPE-1,3-diaminopropane
12	0.76	7.76	
13	0.81	15.73	
14	0.87	12.63	
15	0.93	2.92	

The polyHIPE reference showed the highest surface area of 102.60-106.00 m²/g for the range of surfactant ratio from 1.18 to 1.33 (recipe 2 and 3). The high surface area can be seen as large quantity of spherical shape with high void on the surface as shown in Figure 4.10. For polyHIPE with hexylamine, the highest surface area appears at surfactant ratio 1.50. The optimum ratio with higher amount of surfactant was slightly increased from the polyHIPE reference (1.18-1.33) because a larger amount of monomers, derived from VBC and hexylamine, required more surfactant quantity. It was noted that the addition of amine into the highly porous

structure of polyHIPE did not change the surface area of the adsorbent. The surface area of the polyHIPE-hexylamine ($88.05 \text{ m}^2/\text{g}$) was very similar to that of polyHIPE reference ($89.38 \text{ m}^2/\text{g}$) at a similar surfactant ratio of 1.5. For the polyHIPE with 1,3-diaminopropane, the highest surface area is only $15.73 \text{ m}^2/\text{g}$ at surfactant ratio of 0.81 which affected by the incomplete spherical shape as shown in the SEM microgram (Figure 4.9).

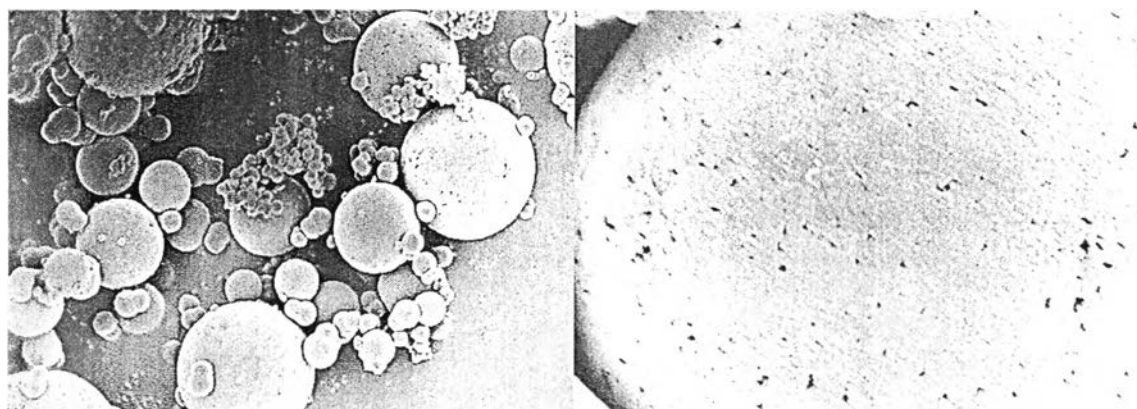


Figure 4.10 SEM micrographs of polyHIPE reference with magnification x10K and x50K surfactant ratio of 1.18.

4.2.2 Amine Loading in PolyHIPE

Since the monomer ratio of DVB to VBC was 9:1 and the conversion of VB-amine according to the reaction of VBC and amine was 51 % in VBC for hexylamine and 56% for 1,3-diaminopropane, there was at most 5% amine in the polyHIPE with respect to the substitution of chloride with amine. Thus, FTIR sensitivity was not high enough to detect amine vibration in the polyHIPE-amine structure. The amount of amine in polyHIPE-amine was measured by CHN analysis as shown in Table 4.4. The polyHIPE reference contains no nitrogen. Percent of nitrogen in polyHIPE-amine was determined from the difference values between polyHIPE-amine and polyHIPE reference, $\Delta \% \text{ N}$. The highest $\Delta \% \text{ N}$ in polyHIPE-hexylamine was 0.44 (recipe 9). PolyHIPE-1,3-diaminopropane showed the highest $\Delta \% \text{ N}$ of 3.8 (recipe 11). It is noted that the surfactant ratio expressed here is the ratio of spanR80 (oil soluble surfactant) to triton-X100 (water soluble surfactant). Lower

surfactant ratio means increase the water soluble surfactant (or decrease the oil soluble surfactant) in the emulsion system, which results in increase amount of oil in water micelle and thus, increases the dissolution of the product derived from VBC and 1,3-diaminopropane in oil leading to high opportunity for polymerization.

Table 4.4 Amine loading measurement

Recipe	polyHIPE	Surfactant ratio	$\Delta\%N$
2	reference	1.18	0
7	-hexylamine	1.20	0.29
8		1.33	0.33
9		1.50	0.44
10		1.71	0.34
11	-1,3-diaminopropane	0.72	3.80
12		0.76	3.67
13		0.81	3.50
14		0.87	2.22
15		0.93	0.75

4.3 Carbon Dioxide Adsorption

The CO₂ adsorption capacities in mmole of CO₂ per grams of adsorbent are measured and shown in Table 4.5. The polyHIPE reference measured is 0.057 mmol/g. While the polyHIPE-hexylamine at the surfactant ratio of 1.50, which provides the most surface area and nitrogen content, gives the highest adsorption capacity, but slightly higher than that of polyHIPE reference. PolyHIPE-1,3-diaminopropane is the lowest surface area, but the adsorption capacity and nitrogen content are the highest among the three types of polyHIPE due to the chemical structure of 1,3-diaminopropane containing 2 amino groups which is higher opportunity to adsorb CO₂. It indicates that the amine in polyHIPE is more effective than surface area. The highest adsorption capacity of polyHIPE-1,3-diaminopropane is 0.377 mmol/g (recipe 11). When the adsorption capacity per unit area (mmole/m²) are compared, polyHIPE reference gives very low value of 0.0005 mmole/m² (recipe 2). While polyHIPE-hexylamine (recipe 7) and polyHIPE-1,3-diaminopropane (recipe 11) are 0.0024 and 0.1287 mmole/m² respectively, that means the polyHIPE-1,3-diaminopropane is the highest effective to adsorb CO₂ per surface area than the

other types because polyHIPE-1,3-diaminopropane contains the most amine for CO₂ adsorption.

Table 4.5 CO₂ adsorption capacity

Recipe	Surfactant ratio	Surface area (m ² /g)	CO ₂ adsorption capacity	
			mmol/g	mmol/m ²
1	1.00	91.28	-	-
2	1.18	106.00	0.0574	0.0005
3	1.33	102.60	-	-
4	1.54	89.38	-	-
5	2.00	65.16	-	-
7	1.20	17.77	0.0436	0.0024
8	1.33	38.75	0.0508	0.0015
9	1.50	88.05	0.0681	0.0007
10	1.71	25.63	0.0561	0.0022
11	0.72	2.93	0.3770	0.1287
12	0.76	7.76	0.2422	0.0312
13	0.81	15.73	0.2225	0.0143
14	0.87	12.63	0.1321	0.0105
15	0.93	2.92	0.0424	0.0145

The polyHIPE-hexylamine were selected to investigate the effect of moisture on CO₂ adsorption ability. The moisturized polyHIPE were taking to measure the quantity of absorbed water and then to determine the CO₂ adsorption capacity. The result is shown in Table 4.6.

Table 4.6 Effect of moisture on CO₂ adsorption capacity of polyHIPE-hexylamine

Recipe	Surfactant ratio	Surface area (m ² /g)	CO ₂ adsorption capacity					wt% water in polyHIPE
			Dried condition		Moisturized Condition		Δ mmol/g dried and moisturized polyHIPE	
			mmol/g	mmol/m ²	mmol/g	mmol/m ²		
8	1.33	38.75	0.0584	0.0015	0.0554	0.0014	-0.0030	35.76
9	1.50	88.05	0.0681	0.0007	0.0445	0.0005	-0.0236	37.69
10	1.71	25.63	0.0561	0.0022	0.0462	0.0018	-0.0099	35.56

The CO₂ adsorption capacity of dried and moisture conditions were compared. All adsorption capacities of moisturized conditions were lower than the dried conditions because the moisture occupied the active sites before adsorbing CO₂. In recipe 9, the highest surface area (88.05m²/g) leads to the most adsorption of water as shown in weight % of water in polyHIPE (37.69 wt%) which results the most decrease in adsorption capacity as expressed in the difference between the dried and moisturized polyHIPE (-0.0236 mmol/g).