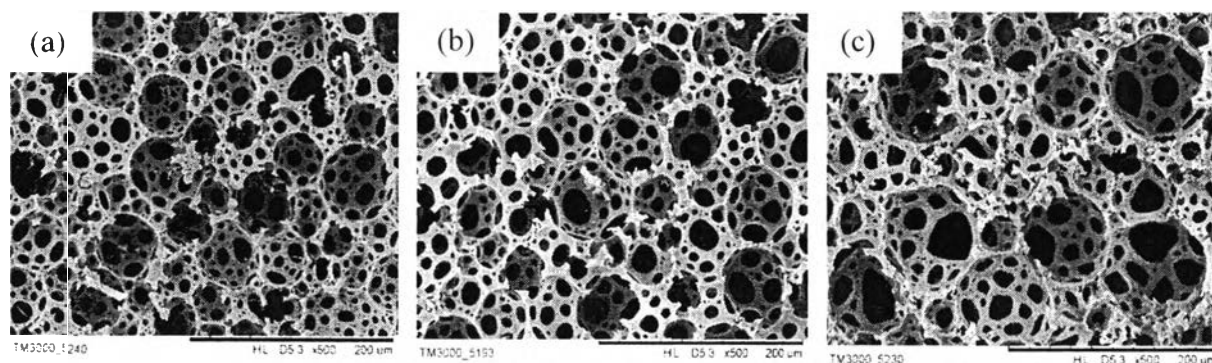


## CHAPTER IV

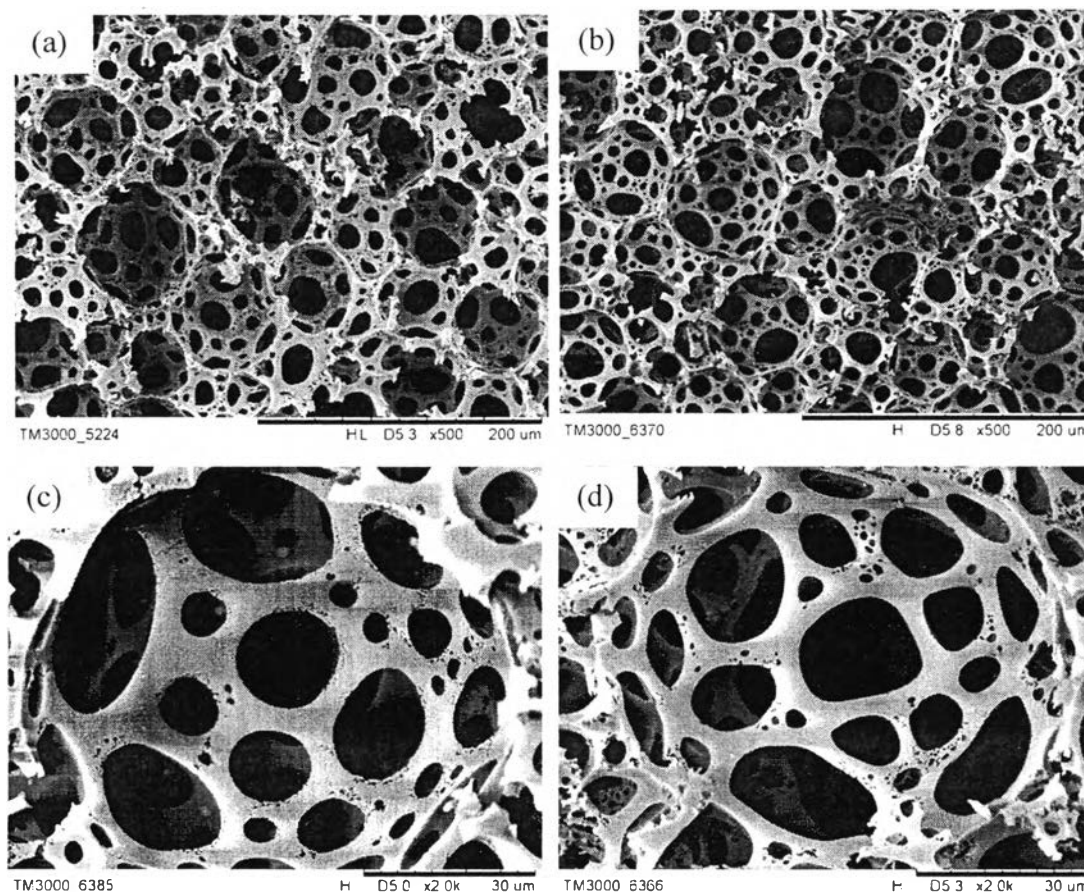
### RESULTS AND DISCUSSION

#### 4.1 Morphology of Poly(S/DVB)HIPE

Normally, the structure of polyHIPEs are meso continuous pores which has interconnecting pore or window (Barbetta *et al.*, 2004). Figure 4.1 provides information about morphology of poly(S/DVB)HIPE using SEM micrographs with magnification  $\times 500$ , prepared by three component surfactant (SPAN80, DDBSS, and CTAB) and difference amounts of styrene and divinylbenzene in the emulsion systems. The pore size diameters of poly(S/DVB) HIPE were found to decreased cell size when increasing in divinylbenzene. For 20 %, 80 %, and 100 % DVB, the average pore diameters of polyHIPE microstructure were 79.4  $\mu\text{m}$ , 58.8  $\mu\text{m}$ , and 41.2  $\mu\text{m}$ , respectively. As a results, decreasing of average pore diameters of poly(S/DVB)HIPE were affected of crosslinking comonomer (DVB). The poly(S/DVB)HIPE system was incorporated more easily when the system was increased divinylbenzene content that the crosslink network formed earlier (Erbay *et al.*, 1999). In addition, poly(S/DVB)HIPE modified surface with amine solution were shown in Figure 4.2, polymer solutions does not closed the pore structure of polyHIPE and it was clearly observe that polymer solutions were coated on the inside of polyHIPE relating to a UV-Vis spectrophotometer testing.



**Figure 4.1** Scanning electron micrographs of different ratio S:DVB of poly(S/DVB) HIPE; (a) 0:100, (b) 20:80, and (c) 80:20



**Figure 4.2** Scanning electron micrographs of poly(S/DVB)HIPE; (a) Unmodified S:DVB 80:20 ( $\times 500$ ), (b) Modified S:DVB 80:20 ( $\times 500$ ), (c) Unmodified S:DVB 80:20 ( $\times 2000$ ), and (d) Modified S:DVB 80:20 ( $\times 2000$ )

#### 4.2 Physical Properties of Poly(S/DVB)HIPE

Surface area of polyHIPEs prepared by using three different ratio of S/DVB i.e. 0:100, 20:80, and 80:20 was measured by an Autosorb-1MP machine. The result shown polyHIPEs had surface area between 456 to 22  $\text{m}^2/\text{g}$  and after amine-modified polyHIPE had surface area of between 360 to 32  $\text{m}^2/\text{g}$ . The surface area of polyHIPE tend to increase with increased amount of DVB in the system as shown in Table 4.1 due to the ability of the high degree of crosslinking (DVB) so the structure becomes more stable (Jin *et al.*, 2006).

**Table 4.1** Surface area and pore size characteristics of poly(S/DVB)HIPE at different S/DVB ratio

(S/DVB) Ratio	Surface Area (m <sup>2</sup> /g) <sup>a</sup>	
	Unmodified Surface	Amine-modified Surface
0:100	456.15±101.89	360.80±122.47
20:80	189.40±16.14	185.50±0.14
80:20	22.39±10.30	32.48±10.01

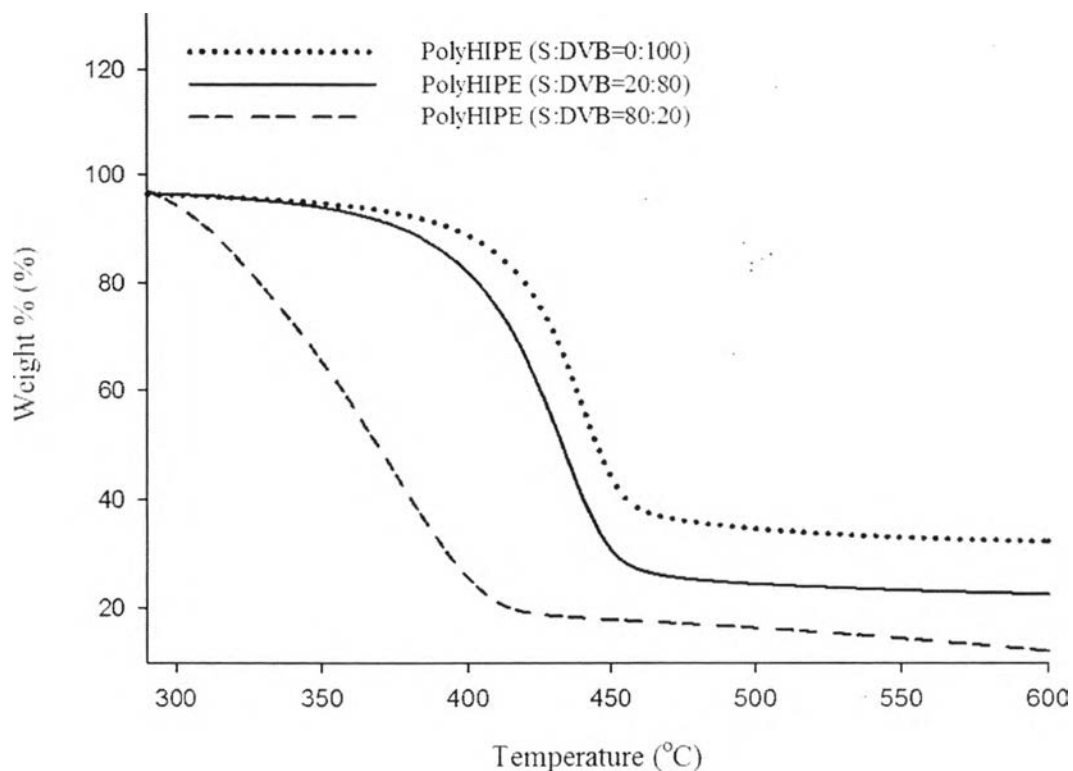
<sup>a</sup>From BET treatment of N<sub>2</sub> adsorption data.

### 4.3 Thermal Properties

Thermal properties of poly(S/DVB)HIPE were investigated by TG analysis. The decomposition temperature ( $T_d$ ) and residue yield of poly(S/DVB)HIPEs was listed in Table 4.2. The result shown  $T_d$  and residue yield were increased with the concentration of divinylbenzene. Due to the high concentration of DVB led to high degree of crosslink so the structure of polyHIPE become more stable (Jin *et al.*, 2006). Normally, material used for CO<sub>2</sub> capture are exposed to temperature in excess of 300 °C so polyHIPEs prepared in this study would be suitable in this application (D'Alessandro *et al.*, 2010).

**Table 4.2** Degradation temperature ( $T_d$ ) and residue yield (%) of poly(S/DVB)HIPE prepared with different S/DVB ratio

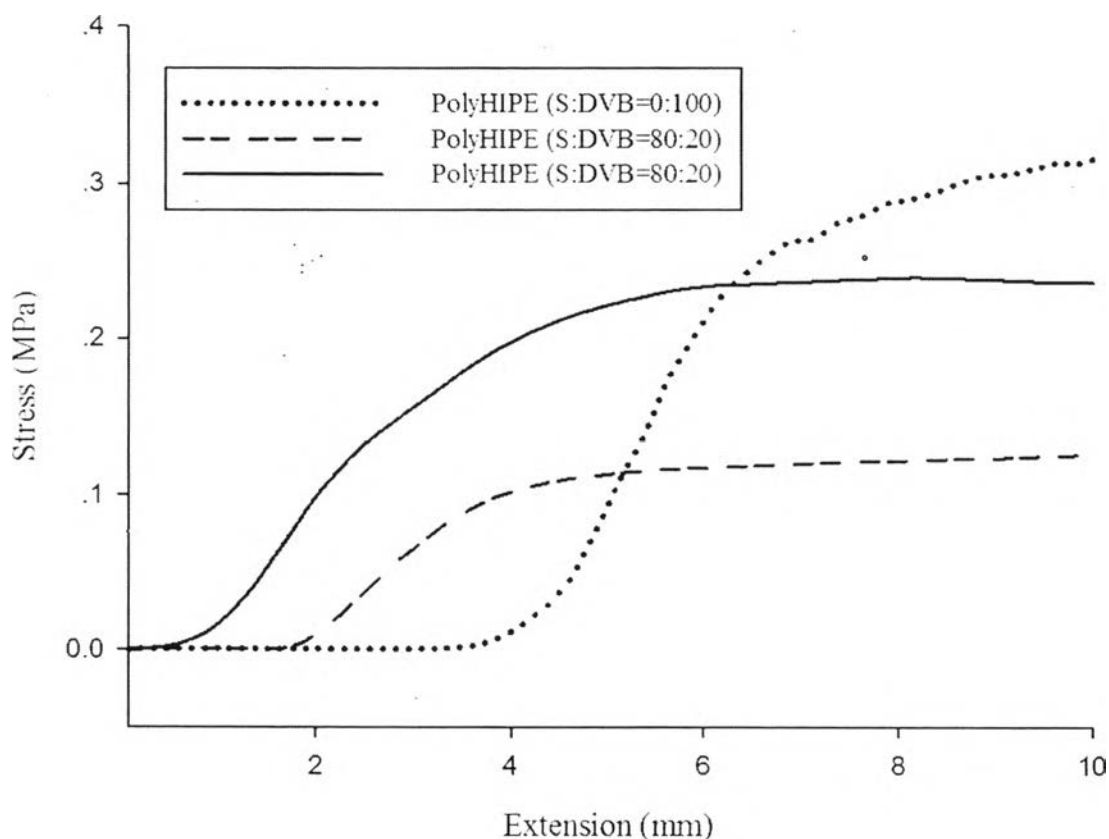
Poly(S/DVB)HIPE	$T_d$ (°C)	Residue Yield (%)
0:100	440.98	32.517%
20:80	432.80	24.816%
80:20	373.79	8.188%



**Figure 4.3** Thermal properties of poly(S/DVB)HIPE prepared with different a ratio

#### 4.4 Mechanical Properties

The mechanical properties of poly(S/DVB)HIPE were studied using LLOYD Universal Testing Machine. The graph of Figure 4.4 provides information about the compressive stress-extension curve for all poly(S/DVB)HIPE, prepared from three component of surfactant with difference amount of S/DVB content. The compressive strength can be calculated by using intersection point between the initial slope and the plateau of the graph.



**Figure 4.4** Compressive stress-extension curves of poly(S/DVB)HIPEs filled with different a ratio

In Table 4.3 gave information on compressive strength (MPa) and young's modulus (MPa) of poly(S/DVB)HIPE. Increasing in divinylbenzene content, the compressive strength was found to increase from 0.13 to 0.30. Young's modulus of sample was increased 1.79-5.41 MPa.

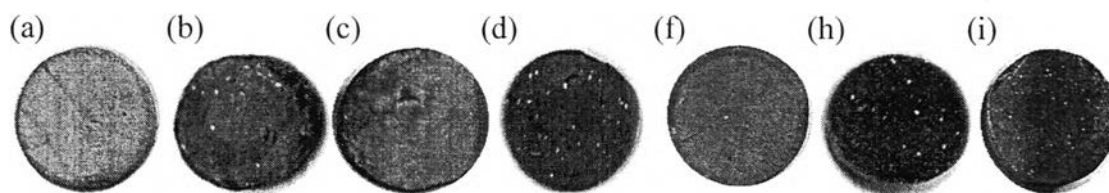
**Table 4.3** Mechanical properties of poly(S/DVB)HIPE between compressive stress (MPa) and young's modulus (MPa) filled with different a ratio

Poly(S/DVB)HIPE	Compressive Strength (MPa)	Young's Modulus (MPa)
0:100	0.30±0.03	5.41±1.29
20:80	0.29±0.09	3.59±1.12
80:20	0.13±0.02	1.79±0.44

The highest compressive strength and young's modulus of poly(S/DVB) HIPE is S/DVB ratio with 0:100 mainly because crosslinking is a strong structure so when increasing amount of DVB in the system polyHIPE become more stable than others (Jin *et al.*, 2006).

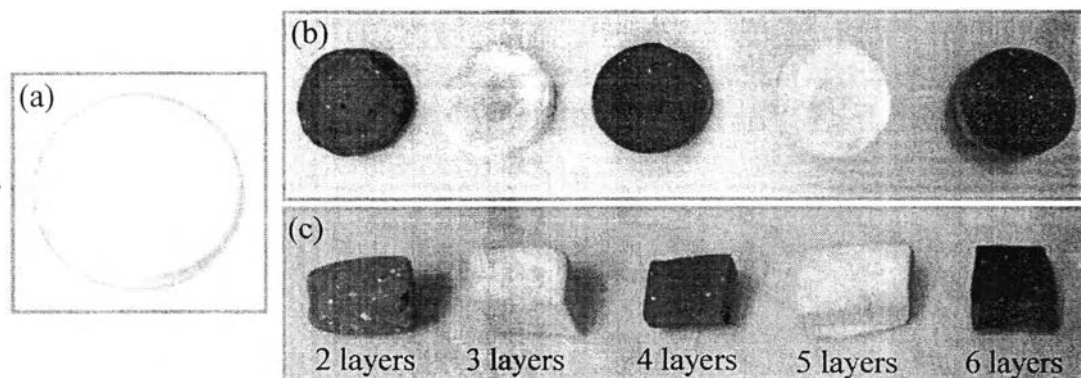
#### 4.5 Surface Modification of Poly(S/DVB)HIPE

Multilayered poly(S/DVB)HIPE was prepared by Layer-by-Layer technique using poly(diallyldimethylammonium chloride) (PDADMAC) and polystyrenesulfonate (PSS). The photograph of polyHIPE modified with PDADMAC at various layers (1, 3, and 5 layers) and PEI by using congo red on top of surface. Furthermore, polyHIPE was modified with PSS at various layers (2, 4, and 6 layers). At the result, the photographs of poly(S/DVB)HIPE with dye are illustrated. The depth of color increases with the number of layers (see Figure 4.5).

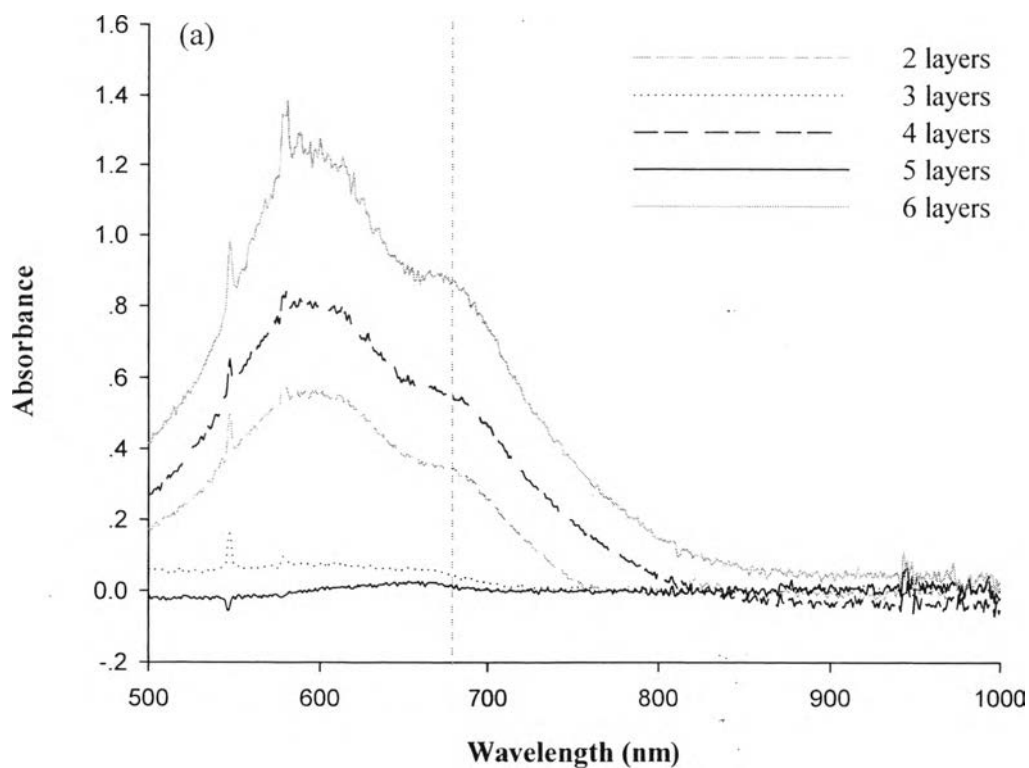


**Figure 4.5** Photograph of polyHIPE modified surface: (a, c, and f) PDADMAC on top of surface ; (b, d, and h) PSS on top of surface and (i) PEI on top of surface

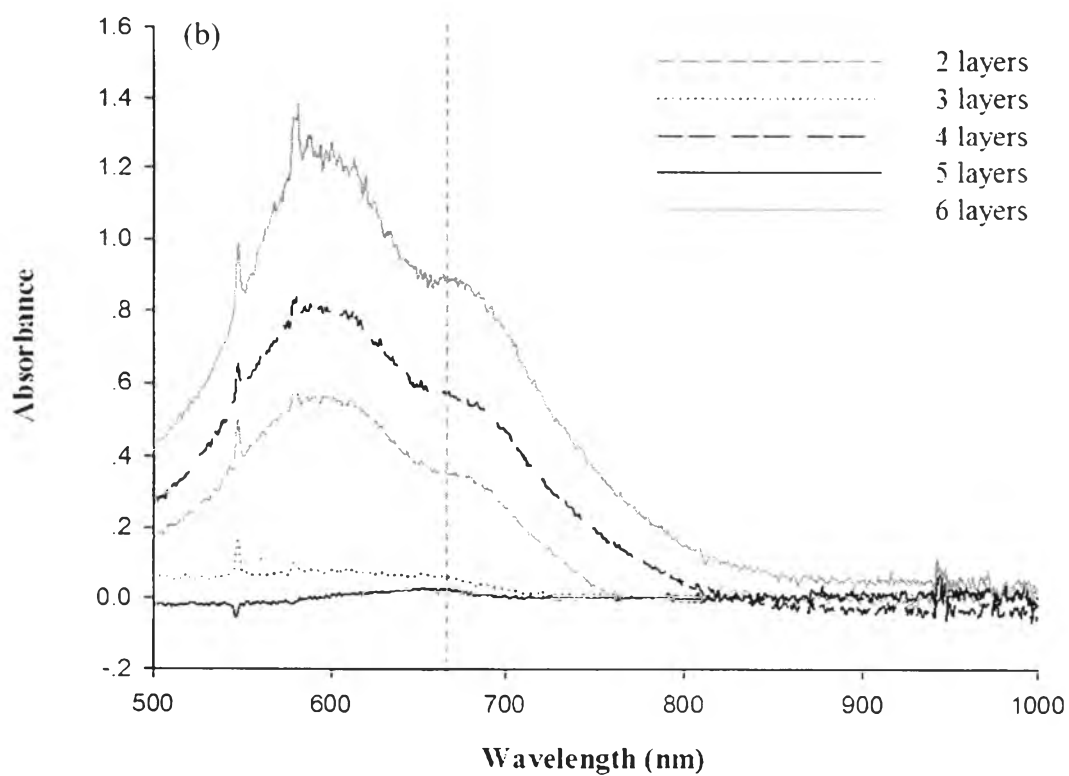
The number of increased layer of the polyelectrolytes for each layer within poly(S/DVB)HIPE was monitored by a UV-Vis spectrophotometer with absorption of light around 670 nm (Figure 4.6). Methylene blue can react with anion, polystyrene-sulfonate (PSS), on surface (2, 4, and 6 layers). The intensity of absorbance increased with the increased of number of layers until six layers. The homogenous coating inside and outside poly(S/DVB)HIPE were confirmed (Figure 4.7 and 4.8). Six layers of PDADMAC/PSS were sufficient to successfully modified on the surface poly(S/DVB)HIPE.



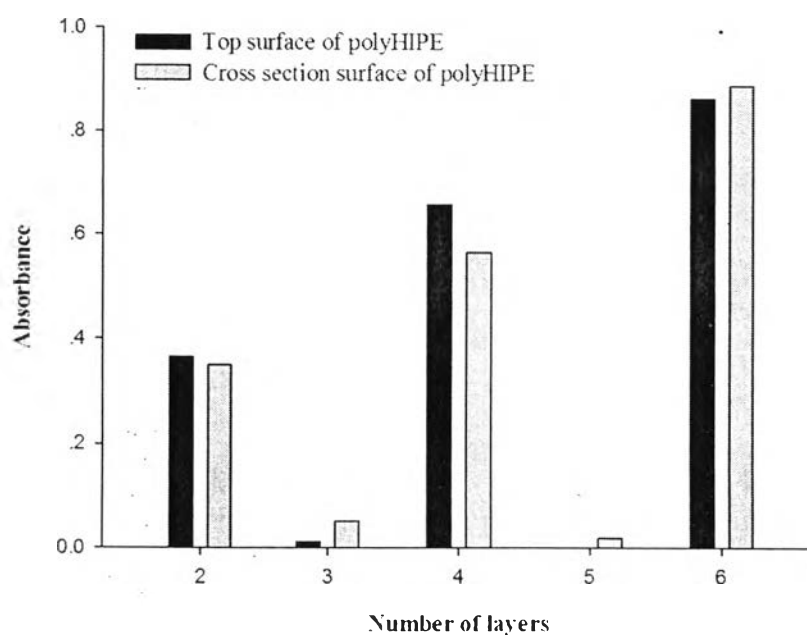
**Figure 4.6** Photograph of polyHIPE modified surface by PDAD-PSS: (a) no coating; (b) surface coating 2 to 6 layers; (c) cross-section coating 2 to 6 layers



**Figure 4.7** Absorbance-Number of layer curves for PDAD/PSS deposited 1.0 M NaCl: (a) Top surface of polyHIPE; (b) cross section of polyHIPE



**Figure 4.7** Absorbance-Number of layer curves for PDAD/PSS deposited 1.0 M NaCl: (a) Top surface of polyHIPE; (b) cross section of polyHIPE (con't)



**Figure 4.8** Absorbance-Number of layer curves for PDAD/PSS deposited 1.0 M NaCl

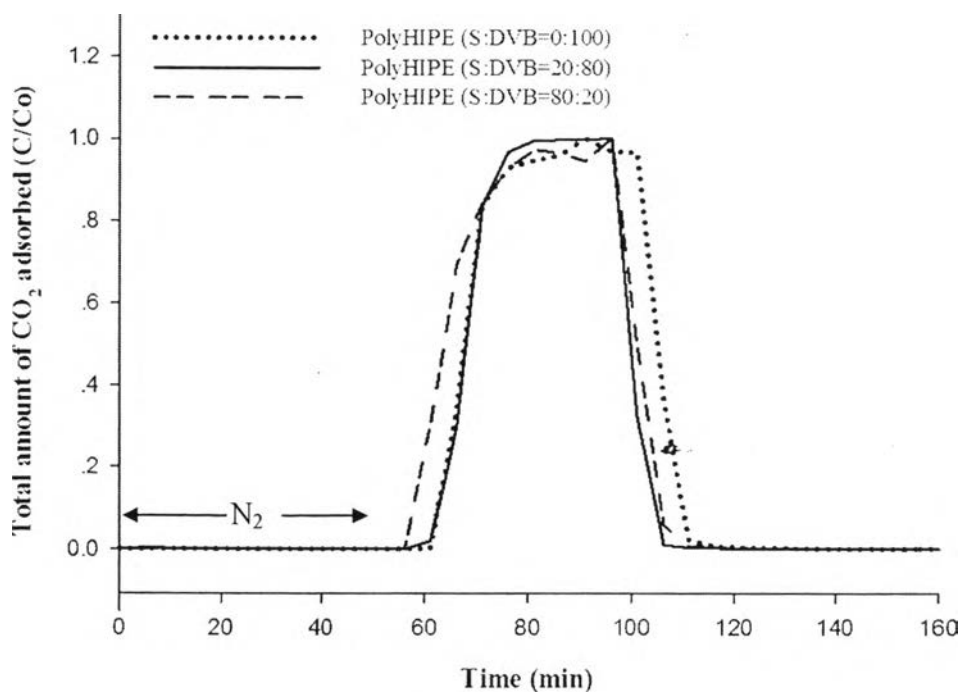


#### 4.6 Adsorption Capacities

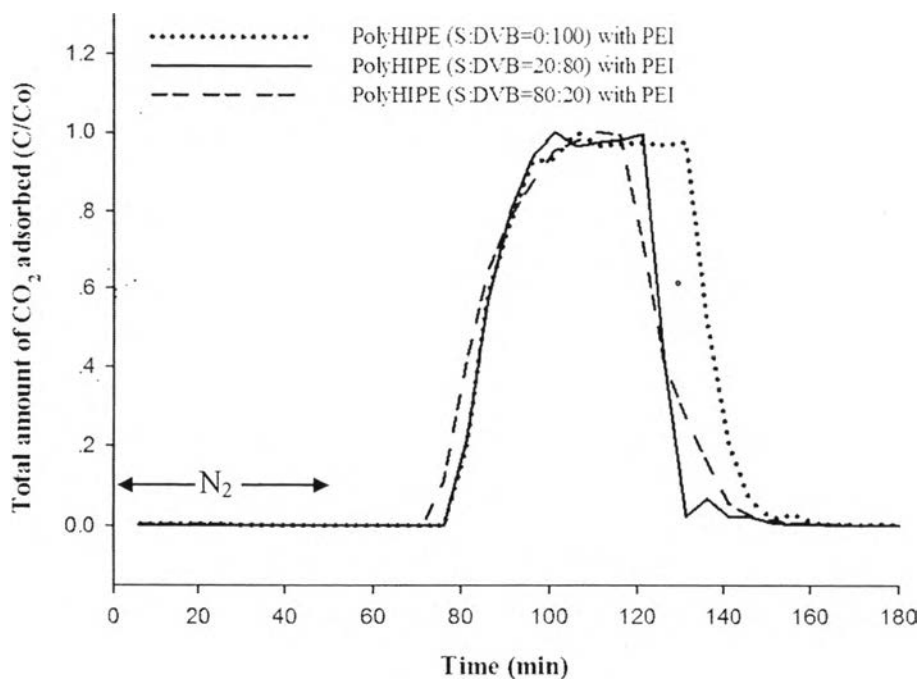
The CO<sub>2</sub> adsorption of neat poly(S/DVB)HIPE and amine-modified poly(S/DVB)HIPE was analyzed. Poly(S/DVB)HIPE was modified by amine solution of polyethylenimine (PEI) and tetraethylenepentamine (TEPA). CO<sub>2</sub> adsorption system was carried out using a mixture gas 15 vol% of CO<sub>2</sub> in N<sub>2</sub> with pressure 30 psi at room temperature. Figure 4.9, 4.10, and 4.11 show the CO<sub>2</sub> breakthrough curve of unmodified and amine-modified poly(S/DVB)HIPEs. Unmodified poly(S/DVB)HIPE at 100 % DVB has slightly higher capacity compared to (S/DVB 20:80) and (S/DVB 80:20) due to the resulting high surface area so polyHIPEs had high physical absorption. Compared to unmodified poly(S/DVB) HIPE, PEI/PSS multilayered poly(S/DVB)HIPE illustrated higher the CO<sub>2</sub> adsorption rate than others due to the ability of chemical adsorption and physical adsorption, both adsorptions lead to high CO<sub>2</sub> adsorption. Table 4.4 provides data about the CO<sub>2</sub> adsorption of poly(S/DVB)HIPE between unmodified and amine-modified poly(S/DVB)HIPE. Significantly, CO<sub>2</sub> adsorption of S/DVB 0:100 modified by PEI had a higher capacity of 1.01 mmol/g. In addition, element analysis results in table 4.7 illustrate the difference in percent of amine by CHN analysis due to effect of adhesive amine on different surface area of polyHIPE. Furthermore, Increasing PDADMAC/PSS multilayers from 2 to 8 layers improved the CO<sub>2</sub> adsorption showed in Table 4.5. However, in this research 6 layers was selected because homogenous coating and CO<sub>2</sub> adsorption have similar value to the 8 layers modification. Finally, PEI/PSS 6 layers modified on surface of poly(S/DVB)HIPE had a higher CO<sub>2</sub> adsorption capacity of 1.04 mmol/g than PDADMAC/PSS multilayers.

**Table 4.4** CO<sub>2</sub> adsorption of poly(S/DVB)HIPE between unmodified and amine-modified surface

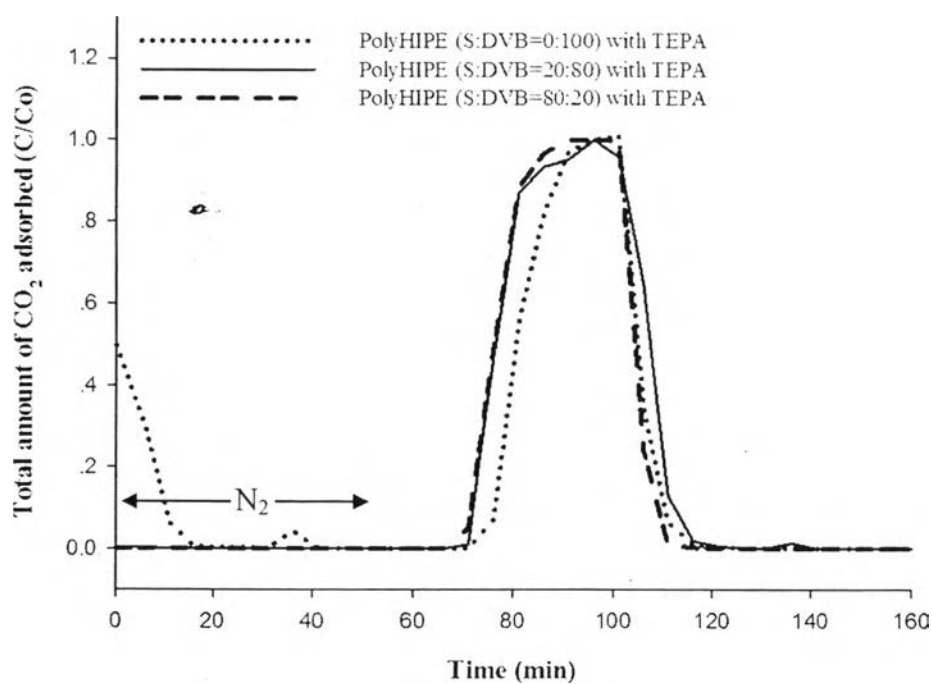
Poly(S/DVB)HIPE	Adsorption Capacity (mmol/g)		
	Unmodified PolyHIPE	Modified PolyHIPE with PEI	Modify PolyHIPE with TEPA
0:100	0.71±0.19	1.01±0.27	0.72±0.11
20:80	0.64±0.12	0.82±0.26	0.72±0.13
80:20	0.63±0.15	0.68±0.16	0.64±0.04



**Figure 4.9** Comparison of the CO<sub>2</sub> breakthrough curve of poly(S/DVB)HIPEs filled with different a ratio



**Figure 4.10** Comparison of the CO<sub>2</sub> breakthrough curve of modified poly(S/DVB) HIPes with PEI



**Figure 4.11** Comparison of the CO<sub>2</sub> breakthrough curve of modified poly(S/DVB) HIPes with TEPA

**Table 4.5** Difference CO<sub>2</sub> adsorption of modify surface of poly(S/DVB (20:80)) HIPEs with difference number of layers

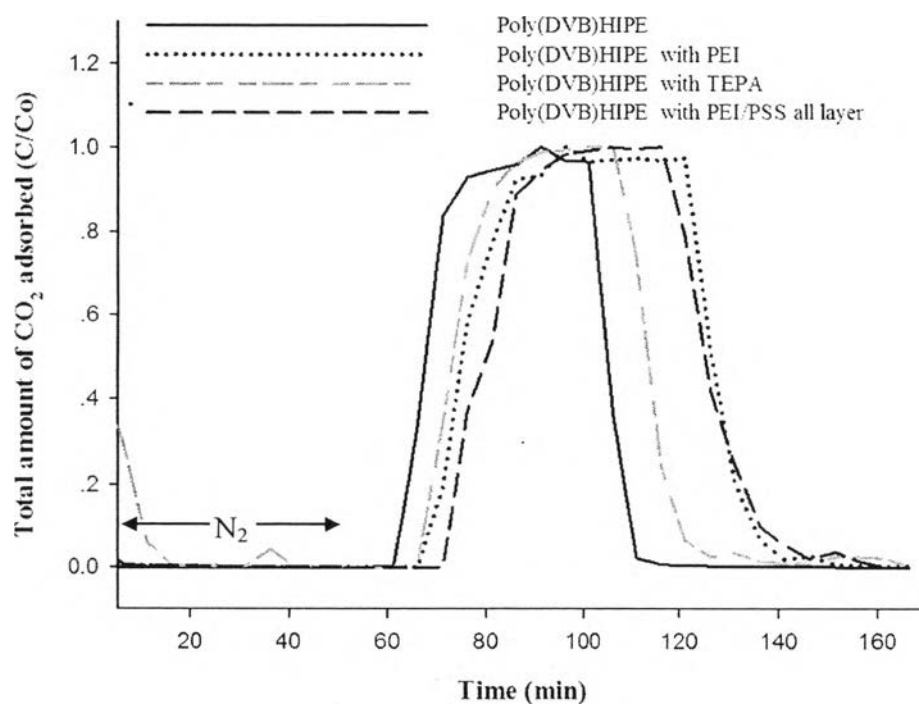
PDADMAC/PSS	CO <sub>2</sub> Adsorption (mmol/g)
2 layers	0.68±0.15
4 layers	0.69±0.10
6 layers	0.82±0.27
8 layers	0.82±0.13

**Table 4.6** CO<sub>2</sub> adsorption of poly(S/DVB)HIPE between unmodified and amine-modified surface

Sample	Adsorption Capacity (mmol/g)
Unmodified polyHIPE	0.71±0.19
Modified polyHIPE with PEI	1.01±0.27
Modify polyHIPE with TEPA	0.72±0.11
Modified polyHIPE with PEI all layers	1.04±0.07

**Table 4.7** Amine content of different samples

Poly(S/DVB)HIPE	Mass Fraction of Nitrogen%	
	Modified polyHIPE with PEI	Modify polyHIPE with TEPA
0:100	0.81	1.54
20:80	0.59	0.52
80:20	0.52	0.56



**Figure 4.12** Comparison of the CO<sub>2</sub> breakthrough curve of unmodified and amine-modified poly(DVB)HIPES