

CHAPTER IV

Highly Porous Material from Poly(S/DVB)polyHIPE Modified by Layer-by-Layer Surface Modification for CO₂ gas Adsorption

4.1 Abstract

A new type of absorbent for CO₂ adsorption was synthesized via emulsion polymerization. The polymer obtained from divinylbenzene (DVB) and styrene (S) at ratio of 0:100, 80:20, 20:80. PolyHIPE were prepared using Span 80: CTAB: DDBSS (6.3 wt%: 0.3 wt%: 0.4 wt%) as surfactants. Poly(diallyldimethyl-ammonium chloride) (PDADMAC) and Polystyrenesulfonate (PSS) and Polyethyleneimine (PEI) was used to modify the surface using the layer-by-layer technique to improve polyHIPE for CO₂ adsorption; the modified polyHIPE were characterized for phase morphology, surface area, thermal behavior, mechanical properties, and CO₂ adsorption by using SEM, N₂ adsorption-desorption, TG-DTA, LLOYD universal testing machine, and CO₂ adsorption, respectively. Phase morphology of poly(S/DVB) exhibited high amounts of DVB showed small pore size and high surface area in N₂ adsorption-desorption testing. The mechanical property, Young's modulus, was increased with increasing amounts of DVB. The sample displayed a mass loss of about 50% and decomposition of the material above 300°C. CO₂ adsorption was 0.000205 mmol/g which high amounts of DVB in monomer ratio. CO₂ adsorption is poor due to the morphology change after modified the surface and The polyelectrolyte does not take place into the pore but take place on the surface.

Keywords: Porous polymer, PolyHIPE, Layer by layer, CO₂ adsorption.

4.2 Introduction

One of the important of life, which causing a problem the most significances is air pollution which comes from many difference sources. The presence its harmful

substances in the atmosphere i.e. nitrogen oxide, particular matter, sulphur dioxide (SO₂), hydrocarbon, carbon monoxide (CO), and carbon dioxide (CO₂), ozone, etc. The industrial activity is mainly environment changes. These substances are toxic to the body and bad effect to our health. Carbon dioxide is considered to be one the major greenhouse gases directly influencing global climate change which contributing in atmosphere is presented on the greenhouse effect. It is estimated that 36% of the United States CO₂ is produced from coal-fired power plants. Therefore Volzone *et al* there are developed adsorbent materials for capture and sequestration of carbon management in the environment. Modification measured at room temperature 25°C and 1MPa (Volzone C. *et al.*,2007).

High internal phase emulsions is a template for preparation of highly porous materials, called polyHIPEs obtained from high internal phase emulsions. An emulsion is described to form oil-in-water (O/W) or water-in-oil (W/O). HIPEs containing an organic continuous (external phase) and an aqueous (internal phase). The volume fraction of the internal phase exceeds 74.05%. The advantages of polyHIPE include highly interconnected open-cell structure, high surface areas, low density down, voids form 10 to 100 µm. and the ability to absorb large volume of liquid (Michael S. *et al.*,2008). One of the most widely used application of polymeric membranes, ion exchange, release system, adsorbents, catalyst support, tissue engineering and scaffold (Lee *et al.*,2004). The most HIPE are generally produced with more hydrophobicity.

The layer-by-layer (LbL) discussed theory and mechanism of charge transfer in polyelectrolyte multilayer films (PEM). Ability of LbL is generating unique material system advantages designing material systems that regulated transport ionic, electronic and molecular species across a polyelectrolyte multilayer membrane. Examples it can exhibit gas transport, using a charged nanomaterial that fully dispersed in water typically dispersion from organic solvent but materials highly surface area (Hammond *et al.*,2011). The layer by layer self-assembly (LbL) controlled thickness and molecular architecture. LbL is low cost process, very stable, environment-friendly. The common LbL method is based on alternating of ionic charges. A result of alternating to immerse of substrate (hydrophobic or hydrophilic)

in a cationic and anionic polyelectrolyte solution (Iost *et al.*,2012). A method is modified surface of hydrophobic polyHIPE to enhance hydrophilicity.

HIPE can adsorbed must be modified by the layer-by-layer that increasing hydrophilicity on surface. In adsorption process, molecules of CO₂ are adsorbed onto a surface of HIPE. On the surface must be have a functional group can be capture or adsorption such as amine functional group. One potential approach for preparing such a sorbent is to graft CO₂ adsorption sites on a high surface area support.

In this work high internal phase emulsion (HIPEs) modified surface that used layer by layer to increase hydrophilicity. Enhancement CO₂ gas adsorption showed high surface area moreover adding amine group on surface.

4.3 Experiment

4.3.1 Materials

Divinylbenzene(DVB; merck) was used as crosslink-comonomer polyHIPE materials. Styrene was supplied from Sigma-Aldrich chemical. Surfactant were used sorbitant monolate (Span 80), dodecylbenzolsulfonic acid, sodium salt (DDBSS), purchased form Sigma-Aldrich chemical and cetyltrimethylammonium bromide (CTAB) supplied form Fluka. Initiator and stabilizer used in experiment were potassium persulphate (K₂S₂O₈, purity ≥ 98% (RT), Fluka) and Calcium chloride (CaCl₂, purity ≥ 97% (KT), Fluka). Toluene (T) was supplied by Lab scan. Polystyrenesulfonate (PSS, sodium salt, MW 70,000), poly(diallyldimethylammonium chloride) (PDADMAC, MW 350,000) and Polyethyleneimine (PEI, MW 2500) were supplied Sigma-Aldrich.

4.3.2 Equipments

4.3.2.1 *Scanning Electron Microscope (SEM)*

Scanning Electron Microscope (SEM) was performed on Hitachi S-4800 (JEOL/JAM 5200 Model to observe surface morphology and pore size of poly(S/DVB)HIPE with ×500 magnifications. Before observation the specimens was cut a small pieces which coated with gold under vacuum to make them electrically conductive.

4.3.2.2 Autosorb-IMP

N₂ adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. The samples were degassed at 110°C for 12 hours in a vacuum furnace before analysis. Surface areas were calculated using the BET equation. Surface area was measured using the dynamic seven points and the isotherm 24 points.

4.3.2.3 Mechanical Properties

Lloyd Universal testing machine was used to measure mechanical properties of all samples in compression mode, according to ASTM D822. Test specimens in a cylinder shape 2.54 cm in diameter × 2.54 cm in height were prepared. A speed of 0.127 cm/min and 500 N load cells were used for all measurements. The value of the compression stress and the Young's modulus were determined from an average of five samples.

4.3.2.4 Thermogravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) was performed to measure the thermal stability of the poly(DVB)HIPE under nitrogen gas atmosphere. The sample was cut into small pieces weigh about 2-5 mg. Then the sample was put into the platinum pan and heated from 30°C to 800°C at a heating rate 10°C/min. The degradation temperature was determined at weight loss from the weight loss vs. temperature curve.

4.3.2.5 Fourier Transform Infrared spectroscopy (FT-IR)

The incorporation of organic group into silicate was investigated by using FTIR. The FTIR was obtained in the frequency range of 400-4000 cm⁻¹ with 32 scans at resolution of 2 cm⁻¹. KBr pellet technique was applied in the preparation of powder samples.

4.3.2.6 Carbon dioxide(CO₂) adsorption

Study of CO₂ gas adsorption capacities of poly(S/DVB)HIPEs at room temperature. The samples were load into sample tube 2×15 cm and were cut a diameter about 2 cm with 1-2 g. CO₂ 15 mL/min and N₂ 85 mL/min were flowed through at room temperature. The amount of CO₂ gas adsorbed by the polyHIPE was determined by Gas Chromatography instrument with Rt®-Q-BOND column with 0.53 mm id x 20 μm film thickness x 30 m length was used to operate at

an isothermal temperature of 40 °C. The GC-TCD injection port was heated to 100 °C with a spilt flow of 8 mL/min and helium as a carrier gas.

4.3.2.7 *Contact angle measurement*

Contact angle measurement was performed by using a Kruss (model DSA 10) contact angle was determined wettability of the surface of poly(S/DVB) polyHIPE. A 10 µL droplet of deionized water was dropped with a micro-syringe onto the polyHIPE surface. Drop shape analysis was explained hydrophilic and hydrophobic for this work.

4.3.3 Experimental Procedures

4.3.3.1 *Preparation of poly(S/DVB)polyHIPE*

HIPE were comprised of aqueous phase and organic phase. HIPE was contained highly pore volume part of aqueous phase (about 90% of total volume) ; deionize water(DI), potassiumpersulphate ($K_2S_2O_8$) as initiator and stabilizer salt ($CaCl_2$). Organic phase containing styrene as monomer divinylbenzene (DVB) as crosslink, porogenic solvent as toluene and mix surfactant (Span 80, CTAB, DDBSS, 6.3 wt%, 0.3 wt%, 0.4 wt%). Preparation poly(S/DVB) was carried out slowly by added aqueous phase into organic phase by stirring approximately 60 minutes with mechanical stirrer at 350 rpm and homogenous time about 10 minutes. The ratio of poly(S/DVB) was showed 0:100, 80:20, 20:80. After finish was taken a material into a glass mold cavity and bring into a water bath at 60 °C for 48 h for polymerization. After all, materials dried in oven at 60 °C for 48 hours or until constant weight. The material was extracted with isopropanol for 6 h and dried in oven at 60 °C unit a constant weight.

4.3.3.2 *Poly(S/DVB)HIPEs Modify surface*

Surface modification by the layer-by-layer polyelectrostatic self-assembly leading to polyelectrolyte multilayers (PEMs) technique. The LbL technique carry out by alternated adsorption between polycation and polyanion. This technique could improve any charged surface and created a hydrophilicity which used for CO₂ adsorption. PEM technique there are 2 type coating consisted of the primary coating and secondary coating. The primary coating was coated between

polystyrenesulfonate (PSS) and poly(diallyldimethyl-ammonium chloride) (PDADMAC). Modification, material was cut a thickness about 2 mm and deposition time of each solution was 2 min. The primer layer was adsorb onto surface by an aqueous solution of PDADMAC concentrated 10 mM in 1 M NaCl and PSS concentrated 10 mM in 1 M NaCl which between them rinsed with DI water. The number of layer in this layer was showed 8 layers. Then the secondary coating was coated between polyethylene imine (PEI) and polystyrenesulfonate (PSS). Deposition was performed-an aqueous solution of PEI concentrated 1M in 1 M NaCl and PSS concentrated 10 mM in 1 M NaCl which between them rinsed with DI water and then them dried in the air. All solution in secondary layer had a charge density in pH 4. The number of layer was exposed 5 layers.

4.3.3.3 *Characterization of Poly(S/DVB)HIPE*

Morphology of poly(S/DVB) polyHIPEs was studied by using scanning electron microscope (SEM).

Surface area analysis of poly(S/DVB) polyHIPEs was measured by using Autosorb-1MP (BET).

Wettability of poly(S/DVB) polyHIPE was investigated by using contact angle.

Identification of chemical property on surface of poly(S/DVB)polyHIPE was determined by fourier transform infrared spectroscopy (FT-IR).

Thermal properties characterizing of Poly(S/DVB)HIPEs was studied by using TG/DTA.

Mechanical properties analysis of Poly(S/DVB)HIPEs was studied by using a Universal Testing Machine (LLOYD).

CO₂ adsorption of poly(S/DVB) polyHIPE was detected by using CO₂ adsorption testing unit.

4.4 Results and Discussion

4.4.1 Preparation of polyHIPE

4.4.1.1 Effect of monomer ratio on polyHIPE properties.

PolyHIPEs with different Styrene/Divinylbenzene were prepared using a surfactant mixture of 6.3 wt% of SPAN 80, 0.4wt% of DDBSS, and 0.3 wt% of CTAB by high internal phase emulsion polymerization. The morphology of poly (S/DVB) was demonstrated open cell structure in different a ratio; 0:100, 80:20, 20:80. Morphology of poly(S/DVB)polyHIPE was show with magnification $\times 500$ in Figure 4.1. When the amount of DVB in the monomer ratio increased, the average pore size diameter increased due to DVB as crosslinking agent. The structure became denser with small pore diameter. The average pore size diameter are shown around 41.60 μm , 60.01 μm and 89.85 μm respectively.

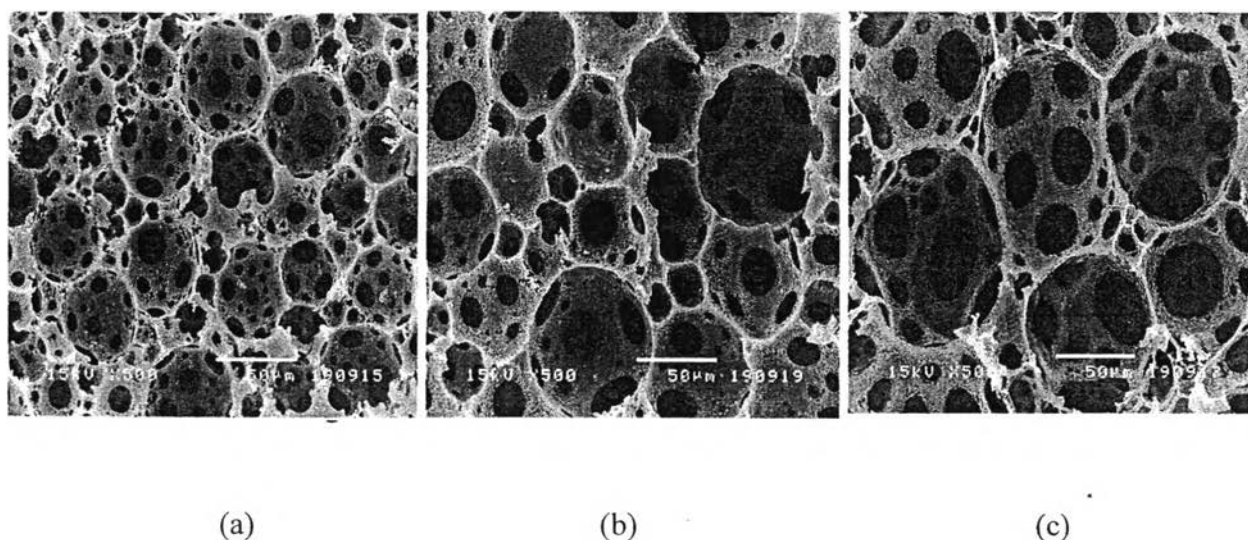


Figure 4.1 SEM micrograph of polyHIPE in different S/DVB ratio of (a) 0:100 (b) 20:80 (c) 80:20.

4.4.2 Surface area of polyHIPE

Surface area properties of polyHIPE were characterized by Autosorb-1MP. When amount of DVB in the monomer ratio increased, the surface area is increased as shown in table 4.1. Therefore monomer ratio has relative to surface area besides be related with pore size diameter. The increased of DVB compared to Styrene probably results in more stable emulsion, giving smaller pore size diameter and high surface area. BET surface area, pore size of polyHIPE were explained in Table 4.1. A typical example of the type of N₂ adsorption/desorption isotherm for polyHIPE filled with different monomer ratio as show in Figure 4.2.

Table 4.1 Surface area and pore size characteristics of polyHIPE in different S/DVB ratio

Poly(S/DVB)	Surface area (m ² /g) ^a	Pore size (μm)
0:100	509.42±35.53	41.60±9.88
20:80	347.50±31.83	60.01±12.28
80:20	5.31±1.18	89.85±8.56

^aFrom BET treatment of N₂ adsorption data.

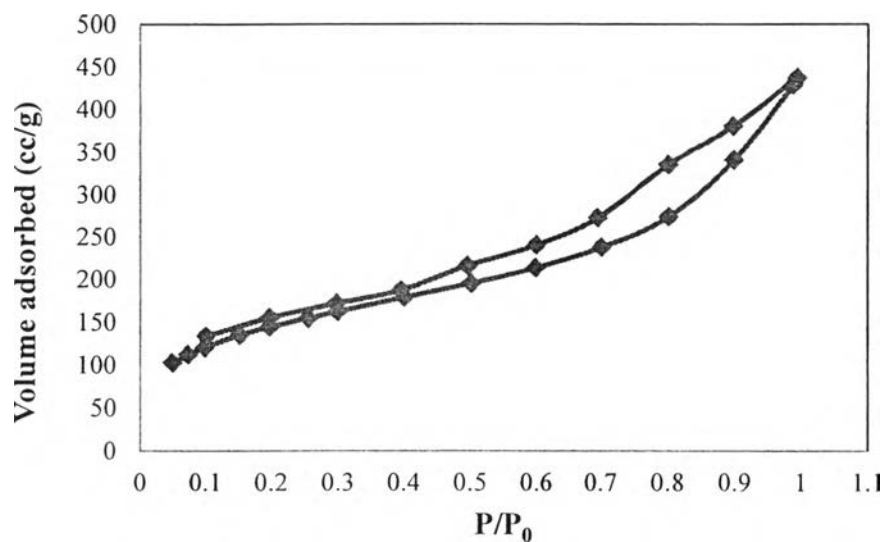


Figure 4.2 A typical example of the type of nitrogen adsorption/desorption isotherm of polyHIPE in different S/DVB monomer ratio of 0:100.

4.4.3 Thermal properties

The thermal behavior of polyHIPE was exterminated with the temperature range 30-800°C and heating rate 10°C/min. TGA thermograms of polyHIPE percent weight loss was presented in Figure 4.3. Degradation temperature (T_d) and residue yield (%) were listed in the table 4.2.

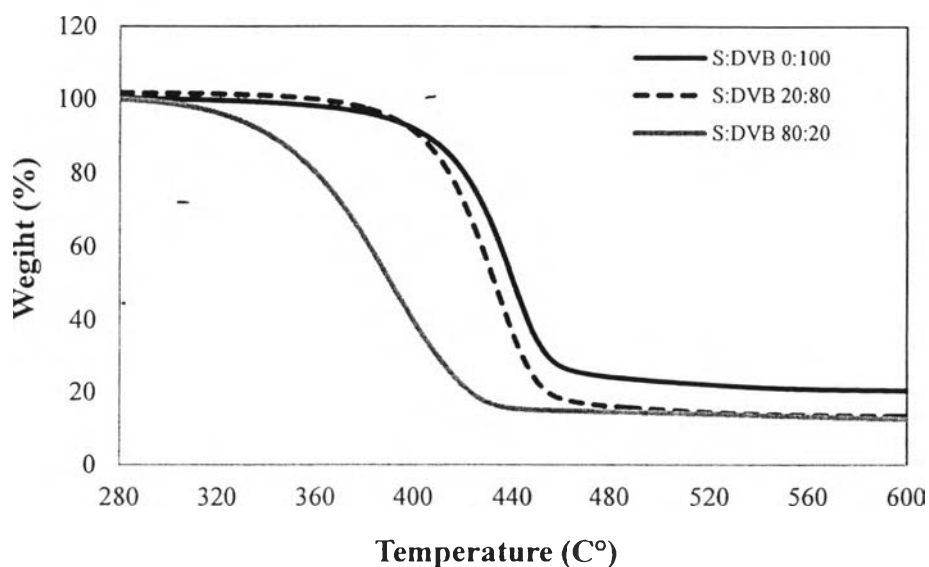


Figure 4.3 TGA thermograms of poly(S/DVB)polyHIPE filled with different a ratio.

Table 4.2 Degradation temperature (T_d) and residue yield (%) of polyHIPE filled with different S/DVB ratio

Poly(S/DVB)HIPE	T_d (°C)	Residue Yield (%)
0:100	430	20.325
20:80	425	13.631
80:20	383	11.068

The degradation temperature of polyHIPE were observed its relationship with amounts of DVB. This result indicated high amount DVB in monomer ratio has highest degradation temperature (T_d). The reason should be related to the structure of divinylbenzene and high degree of crosslinking which difficult to break. The different S/DVB ratio of 0:100, 80:20, 20:80 displayed a mass loss of about 80%, 87%, 89%, respectively and decomposition of the material above 300°C.

4.4.4 Mechanical properties

Mechanical properties of polyHIPE were filled with different S/DVB ratio, carried out by loaded of 70 percent of strain. The compressive strength (MPa) and young's modulus (MPa) were listed in table 4.3.

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

Poly(S/DVB)HIPE	Compressive strength (MPa)	Young's Modulus (MPa)
0:100	0.29±0.07	6.37±1.56
20:80	0.28±0.05	5.71±0.37
80:20	0.31±0.08	2.52±0.54

Compressive strength was exhibited not significant different and Young's Modulus highest at high amounts of DVB. The reason should be related to

structure of divinylbenzene which divinylbenzene as a crosslinking agent. Therefore the material was presented strong sample.

4.4.2 Surface modification of poly(S/DVB)polyHIPE

4.4.2.1 Determination of LbL on polyHIPE

Determination surface how number of layer, carried out to modify added charge on surface until optimum point. The number of layer on surface for PDADMAC and PSS has obtained optimum color not change at 8 layers. The optimum number of layer for PEI and PSS has obtained at 5 layers. The number of layer of poly(S/DVB)polyHIPE was plotted in figure 4.4 and 4.5. The photograph of polyHIPE were modified of PDADMAC and PSS of various layers (0, 1, 3, 5, 7, and 9) by using indigo dye on top of surface in Figure 4.6. The photograph of polyHIPE were modified of PEI and PSS of various layers (0, 1, 3, 5, 7, and 9) by using indigo dye on top of surface in Figure 4.7.

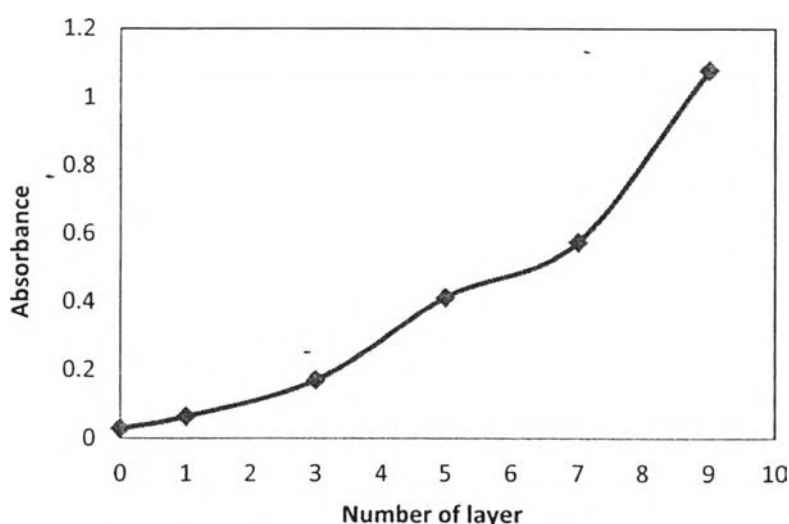


Figure 4.4 Absorbance vs number of layer for PDAD/PSS deposited 1.0 M NaCl.

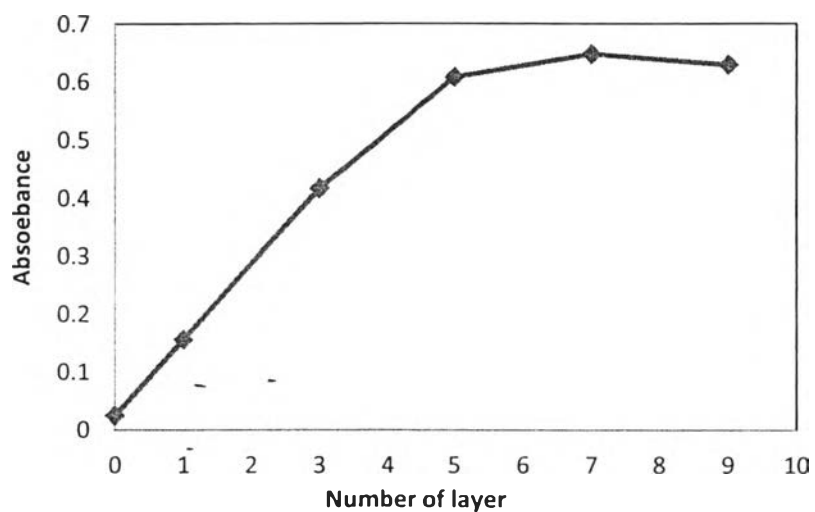


Figure 4.5 Absorbance vs number of layer for PEI/PSS deposited from 1.0 M NaCl.

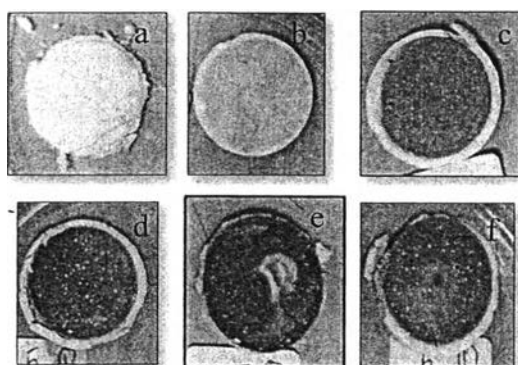


Figure 4.6 Photograph of polyHIPE modified surface of PDADMAC-PSS a) no coating, b) 1 layer, c) 3 layers, d) 5 layers, e) 7 layers and f) 9 layers.

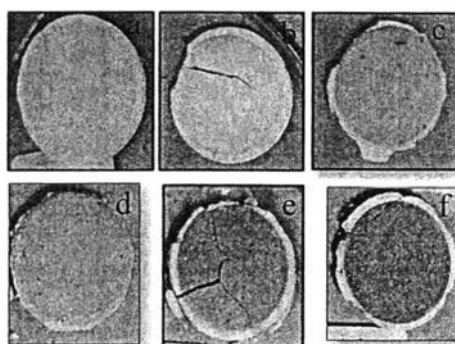


Figure 4.7 Photograph of polyHIPE modified surface of PEI-PSS a) no coating, b) 1 layer, c) 3 layers, d) 5 layers, e) 7 layers and f) 9 layers.

4.4.2.2 The effect wettability of layer by layer on polyHIPE

PolyHIPE are generally produced with hydrophobic due to the structure having a benzene ring group. PolyHIPE correspond to low wettability, while large contact angle ($\geq 90^\circ$). The modification of polyHIPE was carried out to enhance wettability on the surface. The results were illustrated more hydrophilic after modified the surface by using layer by layer technique in table 4.4. A contact angle less than 90° indicate that wetting of surface is favorable, and water can spread over a large area on the surface in figure 4.8. therefore the layer by layer technique can improved to modify surface functional group of polyHIPE.

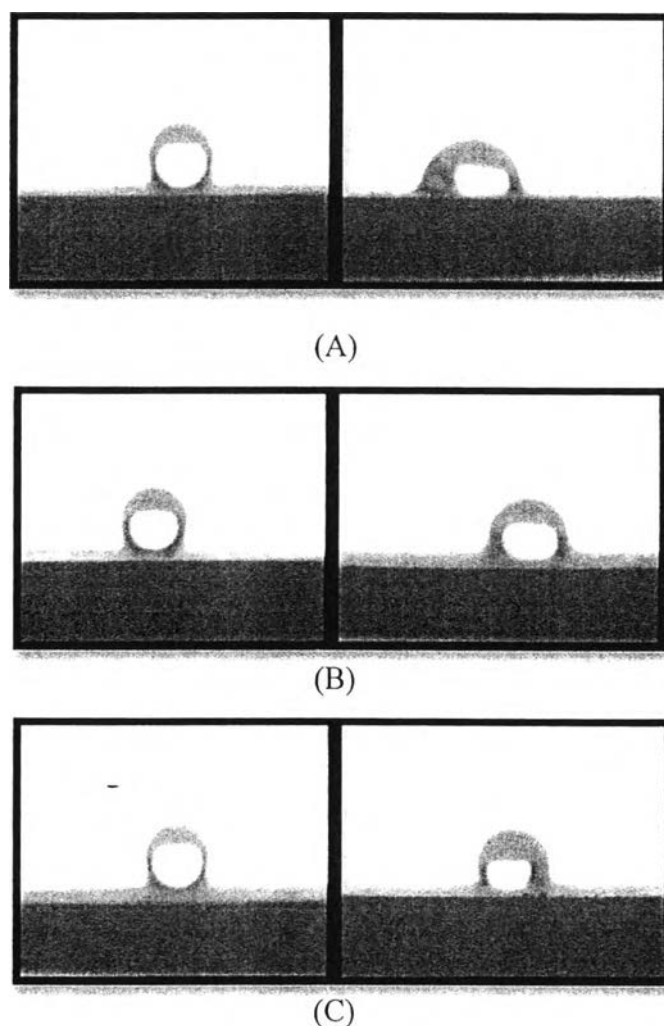


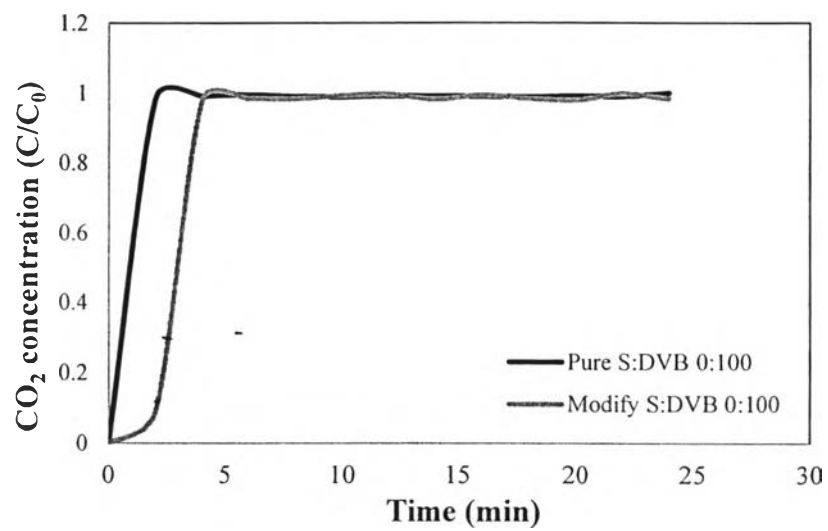
Figure 4.8 Photographs of water droplets before and after polyHIPE filled with different S/DVB ratio of (A) 0:100, (B) 20:80, and (C) 80:20.

Table 4.4 Contact angle of polyHIPE fixed with different S/DVB before and after modified by using LbL technique

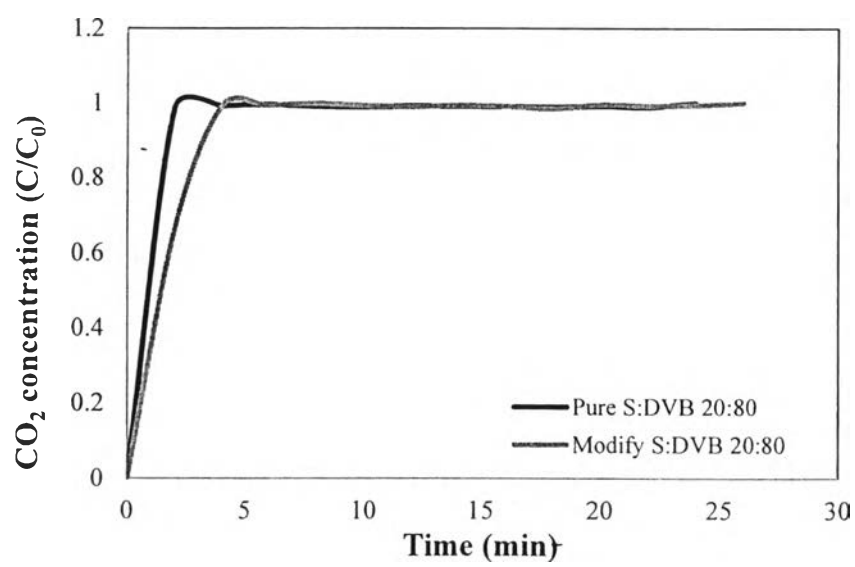
Poly(S/DVB)polyHIPE	Before modified (θ)	After modified (θ)
0:100	130	75
20:80	135	80
80:20	141.5	90

4.4.3 Adsorption capacities

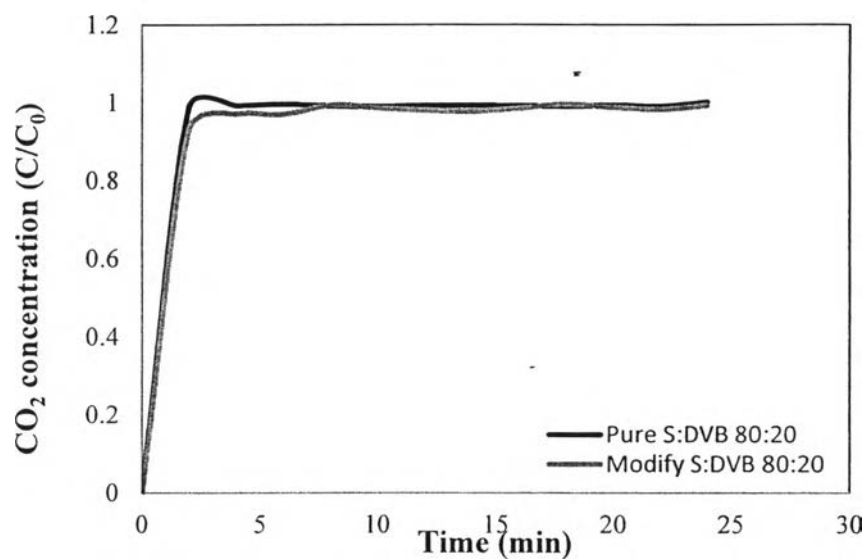
CO₂ adsorption of poly(S/DVB)polyHIPE were carried out a mixture gas between CO₂ 15 ml/min (flue gas condition) and N₂ 85 ml/min with gas chromatography TCD detector at room temperature. A sample of 1 g was loaded of poly(S/DVB)polyHIPE was loaded onto the surface and tested at room temperature. Difference CO₂ adsorption of unmodified and modified surface of Poly(S/DVB)polyHIPE was displayed in table 4.5. Comparison of the CO₂ breakthrough of poly(S/DVB)polyHIPE is presented in figure 4.9. In general, the factor is not enough a function group for CO₂ adsorption. However, loading on the surface can be limited density, concentration, salts, time, and pressure which leads to a relatively CO₂. The reason for CO₂ adsorption of poly(S/DVB)HIPE, the morphology of poly(S/DVB)HIPE which changing after modified the surface as show in figure 4.10.



(A)



(B)



(C)

Figure 4.9 Comparison of the CO₂ breakthrough curve of polyHIPE filled with different S/DVB ratio of 0:100, 20:80, 80:20. Operation condition: weight of adsorbent: 1 g; feed composition: CO₂ 15 ml/min, and N₂ 85 ml/min; temperature: 25°C.

Table 4.5 CO₂ adsorption of polyHIPE filled with different S/DVB ratio

Poly(S/DVB) HIPE	CO ₂ adsorption(mmol/g)		% CO ₂ adsorption
	Unmodified	Modified	
0:100	0.00014±7.24473E-06	0.000345±1.18794E-07	146.43
20:80	0.00014±2.07465E-05	0.000175±1.33679E-05	25.00
80:20	0.00014±5.506E-06	0.000160±1.9467E-05	14.29

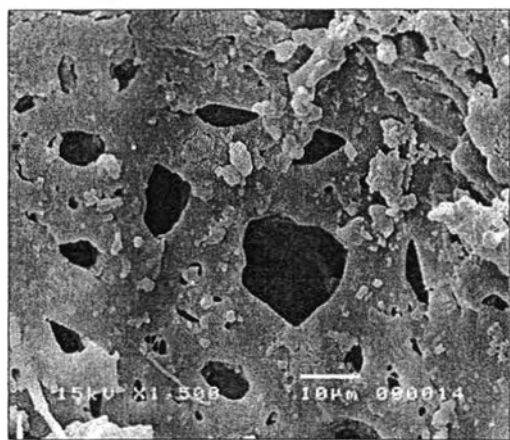


Figure 4.10 SEM micrograph of polyHIPE after modified the surface.