

**CHAPTER IV**  
**CO<sub>2</sub> GAS RETENTION BY POLY(DVB)HIPE POROUS**  
**FOAM FILLED WITH ACID-TREATED ORGANO-MODIFIED BENTONITE**

**4.1 Abstract**

Poly(Divinylbenzene)HIPE was successfully prepared by varying the composition of three surfactants —SPAN80, DDBSS, and CTAB— in a series of five mixed ratios —4.3:0.4:0.3, 6.3:0.4:0.3, 7.8:0.4:0.3, 9.3:0.4:0.3, and 11.3:0.4:0.3, respectively— using acid-treated organo-modified bentonite (0 and 10 %wt) as inorganic reinforcement to elevate the surface area and mechanical properties of the poly(DVB)HIPE for use as an adsorbent for CO<sub>2</sub> gas adsorption. The obtained polyHIPEs were characterized for phase morphology, surface area, thermal properties, and mechanical properties by using SEM, BET, TG/DTA, and a LLOYD universal testing machine, respectively. The surface area and mechanical properties of the resulting materials were found to be dependent on the composition of the mixed surfactant and the acid- treated organo-modified bentonite. The CO<sub>2</sub> gas retention of both polyHIPE filled with acid-treated organo-modified clay and pure polyHIPE foam were also studied using GC. It was found that the suitable % total surfactants for CO<sub>2</sub> gas retention was 7% for pure polyHIPE and 10% for polyHIPE filled with acid-treated organo-modified clay, respectively. With this two mixed surfactants, surface areas of 541 m<sup>2</sup>/g (for the pure PolyHIPE) and 638 m<sup>2</sup>/g (for the filled PolyHIPE) were obtained, along with CO<sub>2</sub> retentions of 13.98 mmol/g and 13.89 mmol/g, respectively.

**Keywords:** Poly(Divinylbenzene)HIPE/ Mixed surfactants/ Acid-treated organo-modified bentonite/ Inorganic reinforcement/ Gas retention

## 4.2 Introduction

PolyHIPE polymers are highly open porous polymeric foams obtained from high internal phase emulsion (HIPE).<sup>[1]</sup> This microporous material has been defined as polymer from the polymerization of an emulsion, where the internal phase occupies more than 70-90% of the total volume. Due to their outstanding properties (such as high porosity, high surface area, and high degree of interconnectivity), the polyHIPE porous foams are considered for many applications such as a scaffold for biomedical applications,<sup>[2]</sup> an ion exchange membrane,<sup>[3]</sup> a filtration media,<sup>[4]</sup> and a catalyst support.<sup>[5]</sup> PolyHIPE materials normally do not have a very high surface area (typically around 20 m<sup>2</sup>/g), while with the addition of more cross-linking agent, the addition of porogenic solvents<sup>[6]</sup> or the addition of mixed surfactants to the monomer phase<sup>[7]</sup> the surface area can rise significantly. Previous studies reported that the use of a mixture of nonionic, anionic, and cationic surfactants led to the increase in surface area and reduce in the cell sizes of PolyHIPE materials.<sup>[7]</sup> This is because of the effectiveness of the mixture of surfactants to form strong interfacial film around each emulsion droplet, leading to the enhance emulsion stability. However the materials with highest surface areas also had a non-cellular morphology and were very weak mechanically. This could be rectified by the addition of inorganic filler to get good mechanical properties. To overcome this problem, acid-treated organo-modified bentonite (by using mainly HCl or H<sub>2</sub>SO<sub>4</sub> solutions)<sup>[8]</sup> is needed to incorporate into the monomer phase of the high internal phase emulsion then the resulting materials with good mechanical properties are obtained.<sup>[9]</sup> It would not only improve the mechanical properties but also would increase the adsorptive capacity of the resulting materials when compared to the unfilled materials.

The purpose of this work is to prepare polyHIPE by varying the composition of three surfactants —SPAN80, DDBSS, and CTAB— in a series of five mixed ratios —4.3:0.4:0.3, 6.3:0.4:0.3, 7.8:0.4:0.3, 9.3:0.4:0.3, and 11.3:0.4:0.3, respectively— using acid-treated organo-modified bentonite (0 and 10 %wt) as inorganic reinforcement to elevate the surface area and mechanical properties of the poly(DVB)HIPE for use as an adsorbent for CO<sub>2</sub> gas which is harmful to the

environment, then determine the suitable composition of three surfactants, and look at the effect on CO<sub>2</sub> gas retention property of the obtained polyHIPE.

### 4.3 Experimental

#### 4.3.1 Materials

Divinylbenzene (DVB) was supplied by Merck. Toluene (T) was supplied by Lab Scan. Isopropanol was supplied by Etalma. Sorbitan monooleate (SPAN80) and Dodecylbenzenesulfonic acid, sodium salt (DDBSS) were supplied by Sigma. Cetyltrimethyl- ammonium [C<sub>16</sub>H<sub>31</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>] bromide (CTAB) was supplied by Fluka. Bentonite (BTN) was supplied by Thai Nippon Chemical Industry Co., Ltd. Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and Calcium chloride dehydrate (CaCl<sub>2</sub>•2H<sub>2</sub>O) were supplied by Fluka.

#### 4.3.2 Methods

##### 4.3.2.1 *Preparation of Poly(DVB)HIPE Filled with Acid-treated Clay*

The cellular materials were prepared by first dissolving organic phase containing 5 mL of DVB monomer, 5 mL of toluene, required amounts of acid-treated clay, and a mixture of nonionic, anionic, and cationic surfactants: SPAN80, DDBSS, and CTAB was added to the mixture, stirred for 10 min. While 90 mL of distilled water containing 0.2 g of potassium persulfate and 1 g of calcium chloride dihydrate were added dropwise. After all the water has been added, the emulsion was further stirred for 20 min and placed in a glass bottle. The obtained emulsions were capped and put in a convection oven at 70°C for 24 h to polymerize. After polymerization, the cellular materials were removed from the glass bottles and washed by soxhlet for 6 h with 2-propanol <sup>[9]</sup>. Then the cellular materials were returned to vacuum oven to dry at 80°C for 48 h.

### 4.3.3 Equipment

#### 4.3.3.1 *Surface Area Analyzer (AS-1)*

N<sub>2</sub> adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 100°C during 12 h in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation.

#### 4.3.3.2 *Thermogravimetric Analysis (TGA)*

Thermo-gravimetric analysis (TGA) was performed to measure the thermal stability of the poly(DVB)HIPE. TGA of both neat and poly(DVB)HIPE nanocomposites were performed using a Perkin Elmer/Pyris Daimond TG/DTA instrument. Experiments were carried out under nitrogen gas atmosphere. Samples were cut into small pieces weigh about 2–5 mg. Then the samples were loaded on the platinum pan and heated to 800° C from 40° C at a heating rate of 10° min/C. One step degradation was observed during testing, and the decomposition temperature was recorded corresponding to 50% decomposition of the material.

#### 4.3.3.3 *Field Emission Scanning Electron Microscope (FE-SEM)*

Field emission scanning electron microscopy was performed on Hitachi S-4800 Model to observe surface morphology of poly(DVB)HIPE. The specimens were coated with platinum under vacuum before observation to make them electrically conductive.

#### 4.3.3.4 *Universal Testing Machine (LLOYD)*

A Lloyds Universal Testing Machine (Lloyds) equipped with a 500 N load cell was used to measure mechanical properties in compression. The samples were loaded at a rate of 1.27 mm/min. Samples of 25.4 mm in diameter and 25.4 mm in height were used for testing of each poly(DVB)HIPE. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached.

#### 4.3.3.5 *CO<sub>2</sub> Gas Adsorption*

Study of CO<sub>2</sub> gas adsorption capacities of poly(DVB)HIPE filled with acid-treated clay were carried out using a pilot gasification unit at the department of Chemical Technology, faculty of Science, Chulalongkorn University.

Samples were cut into small pieces weigh about 1–2 g. Then the samples were loaded into sample tube 2×25 cm. CO<sub>2</sub> 3 mL/min and He 17 mL/min were flowed through the sample at room temperature. The residue of CO<sub>2</sub> was measured by a Gas Chromatography instrument, column used Shimadzu 2014, flow rate 35 mL/min.

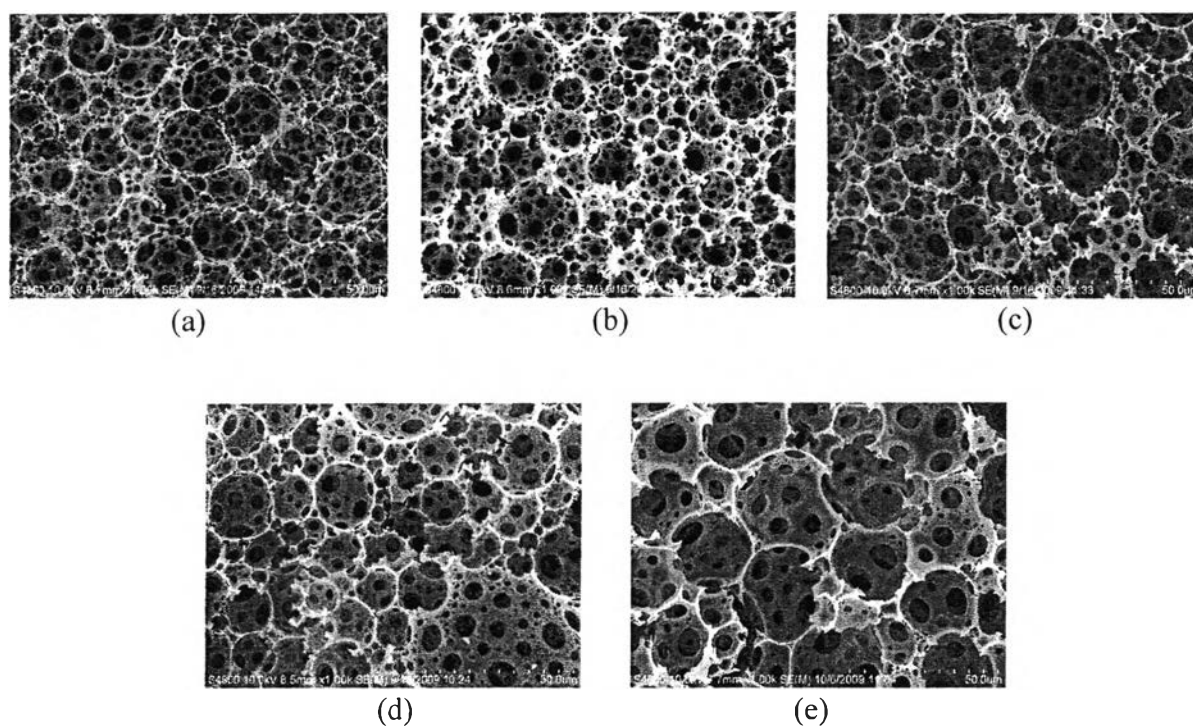
## 4.4 Results and Discussion

### 4.4.1 Characterization of Poly(DVB)HIPE Filled with Acid-treated Clay

#### 4.4.1.1 *Morphologies and Surface Areas*

Morphological characteristics of neat poly(DVB)HIPE (SDCC0) prepared without acid-treated clay filled with different composition of nonionic surfactant, have been investigated by FE-SEM. Micrographs are shown in Figure 4.1.

The number and size of large voids increased with increasing mixed surfactant ratio. This may due to the formation of a poor interfacial film around the emulsion droplet (repulsion between nonionic surfactant) results in the system of poly(DVB)HIPE becoming unstable. This observation was supported by surface area measurement which showed a decreased in surface area when the non-ionic surfactant was more added (listed in Table 4.1).



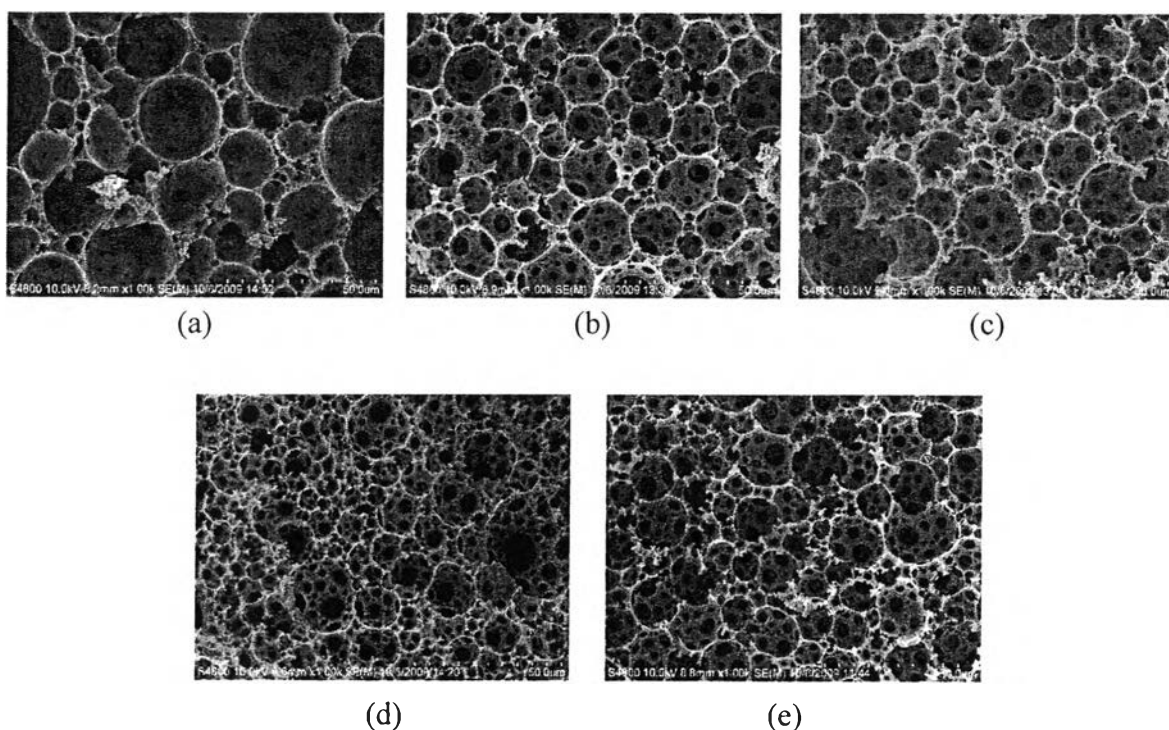
**Figure 4.1** FE-SEM micrographs of SDCC0 filled with different composition of % total surfactant; (a) 5 (4.3 nonionic surfactant); (b) 7 (6.3 nonionic surfactant); (c) 8.5 (7.8 nonionic surfactant); (d) 10 (9.3 nonionic surfactant); and (e) 12 (11.3 nonionic surfactant).

**Table 4.1** Surface areas of SDCC0 filled with different composition of nonionic surfactant (wt%)

% Total surfactant	Surface area (m <sup>2</sup> /g)
5	454 ± 12
7	541 ± 0.28
8.5	403 ± 2
10	256 ± 11
12	134 ± 18

In 2008, Pakeyangkoon *et al.* studied the effect of acid-treated clay to elevate the surface area and mechanical properties of poly(DVB)HIPE for use as an adsorbent for CO<sub>2</sub> gas adsorption by incorporating the acid-treated clay into the monomer phase of the high internal phase emulsion, preparing single surfactant (SPAN80) found that CO<sub>2</sub> gas adsorption capacity increased when acid-treated clay was added.

The changes in different acid-treated clay content, prepared using acid-treated clay 10 wt% (SDCC10) filled with different composition of nonionic surfactant, can be explained using FE-SEM micrographs of the obtained poly(DVB)HIPE (see Figure 4.2).



**Figure 4.2** FE-SEM micrographs of SDCC10 filled with different composition of % total surfactant; (a) 5 (4.3 nonionic surfactant); (b) 7 (6.3 nonionic surfactant); (c) 8.5 (7.8 nonionic surfactant); (d) 10 (9.3 nonionic surfactant); and (e) 12 (11.3 nonionic surfactant).

The number and size of large voids were found to decrease with increasing mixed surfactant ratio. This might be due to the sufficiency of non-ionic surfactant for stabilize emulsion droplet after stabilize acid-treated clay which resulted in the system of poly(DVB)HIPE becoming more stable. Furthermore the acid

treatment of clay minerals removed the octahedral layer cations of bentonite clay, resulting in increasing in porosity and acidity of bentonite clay, leading to higher surface area. This observation was supported by surface area measurement which showed an increased in surface area when the nonionic surfactant was more added (listed in Table 4.2).

Table 4.2 shows that surface area of SDCC10 was depended on mixed surfactant ratio (non-ionic surfactant). At low % total surfactant, the results indicated that non-ionic surfactant was insufficient to stabilize the system. The surface area of polyHIPE which added nonionic surfactant was lower than 10 due to the system of poly(DVB)HIPE becoming unstable.

At 12 % total surfactant, surface area decreased. This was probably due to emulsion becoming unstable and the void size of poly(DVB)HIPE increased (See Figure 4.2) also the amount of nonionic surfactant was too high, resulted in repulsion between nonionic surfactant.

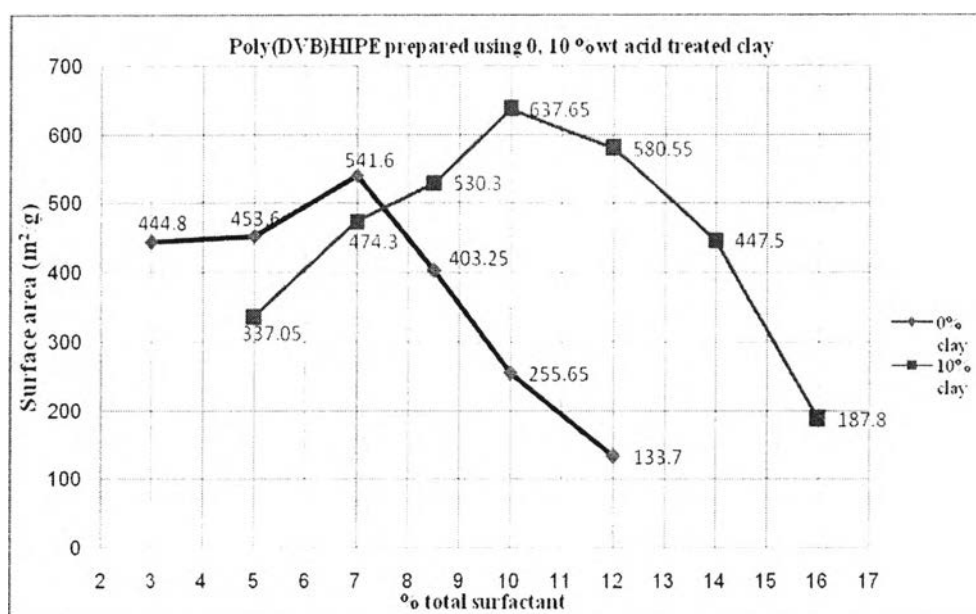
**Table 4.2** Surface areas of SDCC10 filled with different composition of nonionic surfactant (wt%)

% Total surfactant	Surface area (m <sup>2</sup> /g)
5	337 ± 13
7	474 ± 23
8.5	530 ± 11
10	638 ± 16
12	580 ± 35

Figure 4.3 represent the relation between surface area and % total surfactant of neat and 10% filled PolyHIPE. The results showed that the surface area of both PolyHIPE filled with 0 and 10 %wt acid-treated clay were highest at % total surfactant of 7 and 10, respectively. The difference in the



optimum mixed surfactant ratio could be due to the different amount of filled acid-treated clay; 10 %wt acid-treated clay in SDCC10 had more clay and was also more part of hydrophilic group than 0 %wt acid-treated clay in SDCC0, therefore the mixed surfactant tended to stabilize on the filled acid-treated clay much more in the SDCC10. Therefore, the optimum % total surfactant was shifted when clay was added.



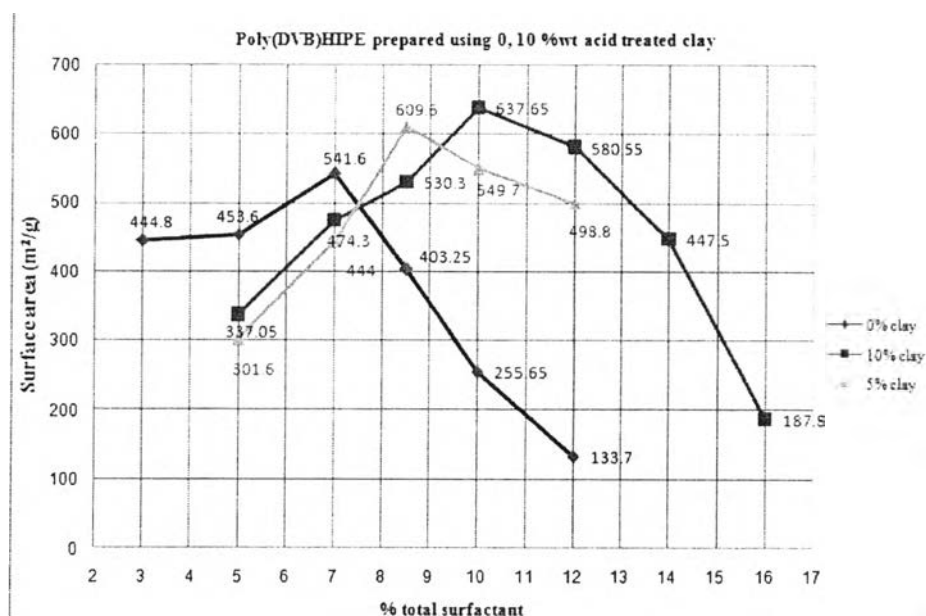
**Figure 4.3** Relation between surface area and % total surfactant of SDCC0, and SDCC10.

For SDCC0 the optimum amount of % total surfactant to achieve the highest surface area was 7 whereas SDCC10 needed 10.

From the figure 4.3, we would like to make sure that the optimum % total surfactant was shifted when clay was added. So, we did another series of 5 %wt acid-treated clay (TDCC5). Surface areas of SDCC5 are shown in table 4.3.

**Table 4.3** Surface areas of SDCC5 filled with different composition of nonionic surfactant (wt%)

% Total surfactant	Surface area (m <sup>2</sup> /g)
5	302
7	444
8.5	610
10	550
12	499



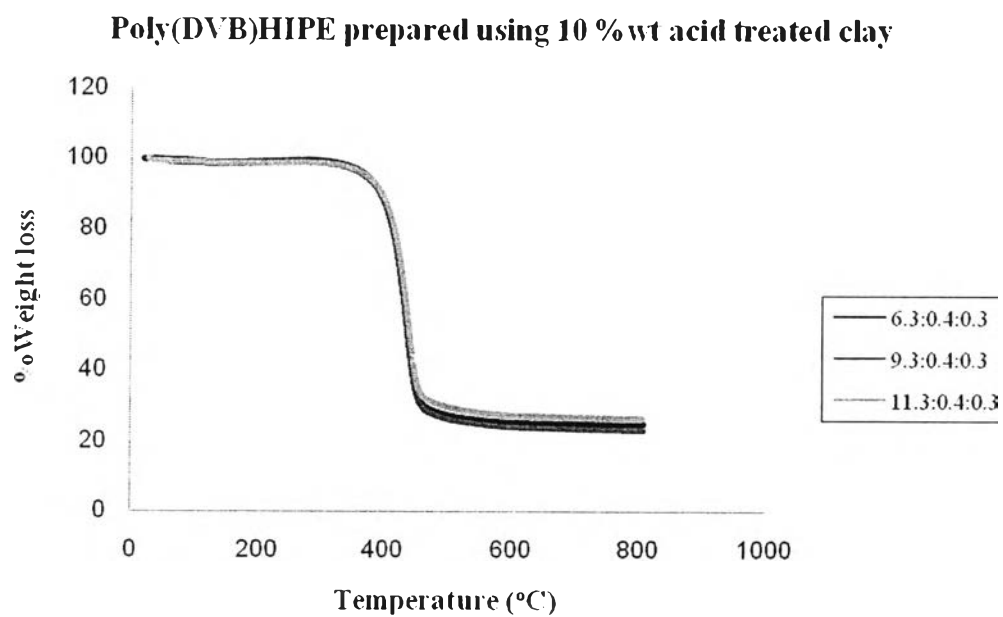
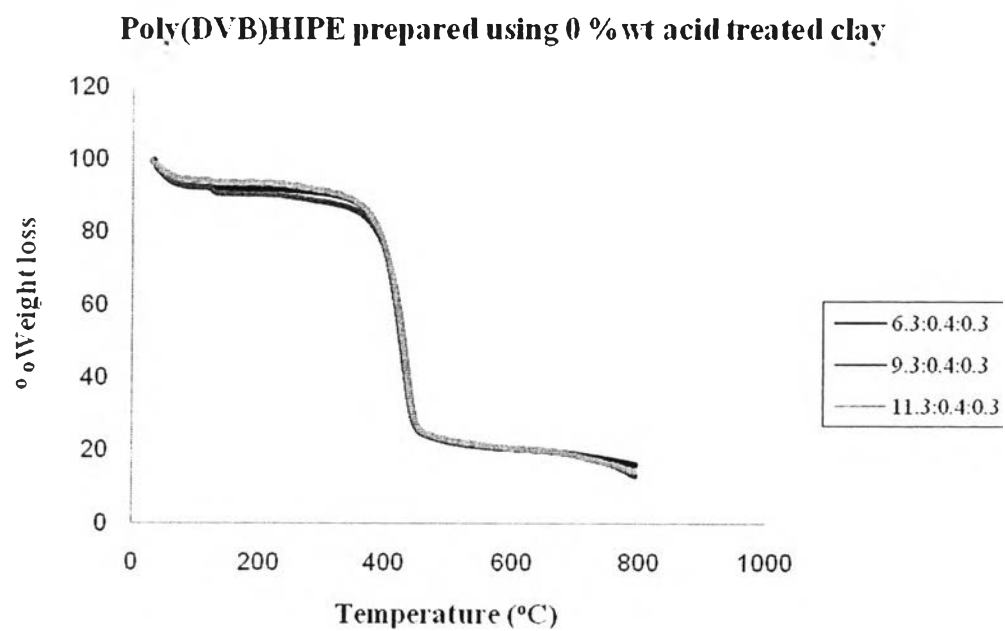
**Figure 4.4** Relation between surface area and % total surfactant of SDCC0,SDCC5, and SDCC10.

Figure 4.4 represent the relation between surface area and % total surfactant of SDCC0, SDCC5, and SDCC10. The results showed that the optimum % total surfactant to achieve the highest surface area for SDCC5 was 8.5 which is between SDCC0 and SDCC10. Therefore, it might possible to

conclude that the optimum % total surfactant was shifted when clay was added.

#### *4.4.1.2 Thermal Properties*

TG analysis of poly(DVB)HIPE, prepared from different composition of nonionic surfactant with(10% wt) and without acid-treated clay, was carried out to measure the thermal stability of the poly(DVB)HIPE with the temperature range between 40-800°C and heating rate of 10°C/min. TGA thermogram of temperature against percent weight loss are shown in Figure 4.5. It was observed from the thermogram that decomposition behaviors of all poly(DVB)HIPE were in the form of a one step degradation process, and hence decomposition temperature reported the temperature corresponding to 50% decomposition of the material. The thermal decomposition temperature ( $T_d$ ) and residue yield (%) were listed in the Table 4.4.



**Figure 4.5** TGA thermograms of (a) SDCC0, and (b) SDCC10.

**Table 4.4** Thermal decomposition temperature ( $T_d$ ) and residue yield (%) of SDCC0 and SDCC10 filled with different composition of nonionic surfactant

%total surfactant	0 % added clay		10 % added clay	
	$T_d$ (°C)	Residue Yield (%)	$T_d$ (°C)	Residue Yield (%)
7	426.11	16.16	438.57	24.73
10	428.51	13.04	438.39	22.79
12	428.22	14.70	441.20	26.21

It was observed that the decomposition temperature of poly(DVB)HIPE nanocomposites shifted to a high temperature (+10 °C) with increasing acid-treated clay from 0 to 10 %wt. Residue yield for poly(DVB)HIPE nanocomposites are higher than neat poly(DVB)HIPE. This result, indicated that the incorporation of clay nanoparticles into poly(DVB)HIPE offers a stabilizing effect against decomposition: protecting from thermal degradation by keeping the polydivinylbenzene chains and the original molecular structure intact which results in increasing decomposition temperature and residue yield of the obtained polyHIPE.

#### 4.4.1.3 Mechanical Properties

##### 4.4.1.3.1 Compressive Response

Mechanical properties of poly(DVB)HIPE, prepared from different composition of nonionic surfactant with(10% wt) and without acid-treated clay, were carried out. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached. The compressive modulus and compressive strength were listed in the Table 4.5.

**Table 4.5** Compressive modulus (MPa) and Compressive strength of SDCC0 and SDCC10 filled with different composition of nonionic surfactant

%total surfactant	0 % added clay		10 % added clay	
	Compressive Modulus (MPa)	Compressive Strength (MPa)	Compressive Modulus (MPa)	Compressive Strength (MPa)
7	2.60±0.21	0.13±0.03	2.79±0.10	0.16±0.01
10	2.56±0.13	0.14±0.02	2.82±0.05	0.17±0.04
12	2.59±0.08	0.13±0.02	2.80±0.11	0.16±0.02

It is observed that poly(DVB)HIPE nanocomposites exhibit higher compressive modulus (+10%) and compressive strength than that of neat poly(DVB)HIPE. This could be due to the ability of organoclay which has high aspect ratio and large surface area of acid-treated clay available for adhesion between polymer matrix and reinforcing phase leading to provide the better stress transfer and contributed to the improvement of mechanical performance.

#### 4.4.1.4 Adsorption Capacities

CO<sub>2</sub> gas adsorption of poly(DVB)HIPE, prepared from different composition of nonionic surfactant with(10% wt) and without acid-treated clay, was carried out using a pilot gasification unit at the Department Chemical Technology Department, Faculty of Science, Chulalongkorn university with flow CO<sub>2</sub> 3 mL/min and He 17 mL/min through the sample at room temperature. The CO<sub>2</sub> gas adsorption capacities were listed in Table 4.6.

**Table 4.6** CO<sub>2</sub> gas adsorption capacity (mmol/g) of SDCC0 and SDCC10 filled with different composition of nonionic surfactant

% total surfactant	0% added clay (SDCC0)		10% added clay (SDCC10)	
	Surface area (m <sup>2</sup> /g)	CO <sub>2</sub> gas adsorption capacity (mmol/g)	Surface area (m <sup>2</sup> /g)	CO <sub>2</sub> gas adsorption capacity (mmol/g)
5	454 ± 12	9.19	337 ± 13	2.46
7	541 ± 0.28	13.98	474 ± 23	7.80
8.5	403 ± 2	8.05	530 ± 11	9.73
10	256 ± 11	4.52	638 ± 16	13.89
12	134 ± 18	4.17	580 ± 35	10.36

The CO<sub>2</sub> gas adsorption capacity of SDCC0 was found to decrease with increasing % total surfactant, but the CO<sub>2</sub> gas adsorption capacity of SDCC10 was found to increase with increasing % total surfactant. This result indicated that the highest adsorption was obtained, when the polyHIPE has the highest surface area.

For the optimum % total surfactant to achieve the highest CO<sub>2</sub> gas adsorption capacity was 7 for SDCC0 whereas SDCC10 needed 10.

**Table 4.7** CO<sub>2</sub> adsorption capacity (mmol/g) on different samples

Samples	CO <sub>2</sub> adsorption (mmol/g)
Neat poly(DVB)HIPE	13.98
10% acid-treated clay poly(DVB)HIPE	13.89
10% organo clay poly(DVB)HIPE	2.68
Activated carbon <sup>[10]</sup>	1.79
Activated carbon treated by Fe <sub>2</sub> O <sub>3</sub> <sup>[10]</sup>	3.06
Activated carbon treated by Cr <sub>2</sub> O <sup>[10]</sup>	3.39
Activated carbon treated by Zn-Fe <sub>2</sub> O <sub>3</sub> <sup>[10]</sup>	2.73

Activated carbon treated by Zn- Cr <sub>2</sub> O <sup>[10]</sup>	2.09
Silicalite <sup>[11]</sup>	2.02
HZSM-5 <sup>[11]</sup>	2.14

When compare poly(DVB)HIPE with other commercial adsorbents, poly(DVB)HIPE with and without acid-treated clay can increase CO<sub>2</sub> adsorbed more than 100% in comparison to other samples. The CO<sub>2</sub> adsorption capacity of commercial adsorbents were listed in Table 4.7.

#### 4.5 Conclusions

Poly(DVB)HIPE porous foam was prepared successfully by varying the composition of three surfactants —SPAN80, DDBSS, and CTAB— in a series of five mixed ratios —4.3:0.4:0.3, 6.3:0.4:0.3, 7.8:0.4:0.3, 9.3:0.4:0.3, and 11.3:0.4:0.3, respectively— using acid-treated organo-modified bentonite (0 and 10 %wt) as inorganic reinforcement. The obtained polyHIPE were characterized for phase morphology, surface area, thermal properties and mechanical properties. Both decomposition temperature (+10 °C) and compressive modulus (+10%) of the resulting materials were improved when 10 wt% acid-treated clay was employed. Highest surface area of both SDCC0 and SDCC10 was achieved when materials were further subjected to use optimum amount of nonionic surfactant. The suitable amount of % total surfactant for CO<sub>2</sub> gas retention was 7% for pure polyHIPE and 10% for polyHIPE filled with acid-treated organo-modified clay, respectively. With this two % total surfactants, surface areas of 541 m<sup>2</sup>/g (for the pure PolyHIPE) and 638 m<sup>2</sup>/g (for the filled PolyHIPE) were obtained, along with CO<sub>2</sub> retentions of 13.98 mmol/g and 13.89 mmol/g, respectively.



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