

CHAPTER VI

HIGHLY POROUS MATERIALS VIA POLYMERIZED HIGH INTERNAL PHASE EMULSION FILLED WITH ORGANO-BENTONITE: SYNTHESIS, CHARACTERIZATION, AND CO₂ ADSORPTION

6.1 Abstract

Three types of organoclay including hybrid organic-inorganic porous clay heterostructure (HPCH), organo-modified bentonite (MOD) and acid treated organo-modified bentonite (AC-MOD) were used as inorganic reinforcement for highly porous polymeric foam (polyHIPE foam). The effect of different type of organoclay on physical properties and CO₂ adsorption capacity of poly(DVB)polyHIPE nanocomposites foam was investigated. By incorporating the organoclay into the monomer phase of the high internal phase emulsion, it would not only improve the surface area, thermal and mechanical properties but also would increase the CO₂ adsorptive capacity of the resulting materials when compared to the unfilled polyHIPE foam. Poly(DVB)polyHIPE nanocomposites foam filled with organoclay was successfully prepared by using high internal phase emulsion process (HIPE) and 0, 1, 3, 5 and 10 %wt of organoclay was also incorporated into continuous phase of polyHIPE polymer to increase the adsorption properties of poly(DVB)polyHIPE nanocomposite and to solve their weak mechanical properties. All polyHIPE nanocomposites foam were characterized for phase morphology, thermal behavior, surface area, mechanical properties and adsorption of CO₂ by using SEM, TG-DTA, N₂ adsorption-desorption, LLOYD universal testing machine and CO₂ adsorption unit, respectively. Phase morphology of poly(DVB)polyHIPE foam filled with organoclay (for all HPCH filled polyHIPE, MOD filled polyHIPE and AC-MOD filled polyHIPE) exhibited similar phase behavior, which showed an open cellular structure with small interconnectivity. In all systems, the surface area and the decomposition temperatures (T_d) for the series of poly(DVB)polyHIPE filled with organoclay increased with increasing clay content from 0 to 10 wt% whereas the

maximum improvement for mechanical properties was observed at 5 wt% of organoclay. The adsorption of CO₂ gas by poly(DVB)polyHIPE foam filled with organoclay was found to increase as well when compared with neat poly(DVB)polyHIPE foam. Additionally, it has been demonstrated in this study that the adsorption of CO₂ by poly(DVB)polyHIPE foam filled with AC-MOD increased by 127% (from 0.0029 to 0.0067 mol/g) compared with neat poly(DVB)polyHIPE foam whereas in the system of poly(DVB)polyHIPE foam filled with HPCH and MOD increased by 63% and 55%, respectively.

Key words: High internal phase emulsion; Poly(DVB)polyHIPE; PolyHIPE; Bentonite; Organo-modified clay; Porous clay; CO₂ adsorption.

6.2 Introduction

Today, air pollution is one of the most important environmental problems. It comes from man-made, industrial activities, power plants, car transport, combustion and gasification process. Air pollution is any chemicals or compounds, consist of carbon monoxide (CO), sulfur dioxide (SO₂), volatile organic compounds (VOCs), lead and carbon dioxide (CO₂). Especially, the main cause is the industrial activities, which are carried out by human. Carbon dioxide (CO₂) is one of the major pollutants in the atmosphere. It is toxic to the body and can be harmful to breathing and other health problems [1]. The formation of huge volume of CO₂ contributes to the creation of the greenhouse effect is presented in the atmosphere like pollutants [2]. To minimize this problem, it is very important to design adsorbent materials that would adsorb such gas before being liberated into the environment. Many scientists developed the adsorbent for gas adsorption in air treatment process i.e. by using zeolites and/or silica as solid adsorbent in gas separation process [3-4]. In 2007, Volzone *et al.* reviewed that clay mineral and their modified products i.e. organo-modified clay and acid treated organo-modified clay can be used as solid adsorbents in gas adsorption technology, which help to remove as much as greenhouse gases and other pollutants to the atmosphere [1].

Currently, highly open porous polymeric foam, obtained from high internal phase emulsions (HIPE process) have attracted in many applications due to their unique characteristics such as high porosity (up to 90 %), high surface area (up to 700 m²/g) and degree of interconnectivity. This porous material so called polyHIPE porous foam which has been defined as emulsions where the internal phase occupies more than 74% of the total volume [5-7]. The continuous organic phase, which generally constitutes less than 26% of the final volume, can contain monomers, crosslinking comonomers and organic soluble surfactant [8]. From the literature reviews, polyHIPE porous foam are being considered for many applications such as a scaffold for biomedical applications [9-12], catalyst support [13], filtration media [14] and ion exchange membrane [15]. Based on excellent characteristics of polyHIPE foam, make it an ideal candidate to be used as adsorbent in the adsorption of such gases. Presently, there are many works attempting to further improve the surface properties of polyHIPE materials. Usage of the three-component surfactant with inert porogenic solvent increase the emulsion stability of the system and high surface properties of the polyHIPE can be obtained when a secondary pore structure is generated within the cell walls of the obtained materials [16-17]. Unfortunately, polyHIPE porous foam has low density, chalkiness and brittleness, poor mechanical performance of polyHIPE foams were also obtained leading to limits their practical use in most industrial applications. More researchers were focused on ways to improve the physical properties of polyHIPE polymer using inorganic materials as a reinforcing agent [18-19]. In a number of investigations, modified clay was found to significantly affect the overall properties of the polymeric composite materials. Modifying clay mineral using ion exchange reaction with quaternary ammonium cations, will result in layered silicates in clay being expanded and the d-spacing of organo-modified clay is increased. After modification, organo-modified clay can be compatible with polymer matrix and play an important role as an inorganic reinforcement [20]. The effect of hybrid organic-inorganic porous clay heterostructure (HPCH), derived from organo-bentonite, which prepared through surfactant-directed assembly of tetraethoxysilane (TEOS)/methyltetraethoxysilane (MTS) into galleries of clay mineral, on the properties of poly(DVB)polyHIPE foam

was reported in previous work. The results showed that the presence of layered silicate in the polymer matrix resulted in the enhancement of mechanical properties of the foams filled with organoclay. Moreover, clay mineral would not only provide reinforcement but also adding new properties; i.e. the incorporation of layered silicate in the polymer matrix should lead to improving the surface properties and thermal stability, of the obtained materials [21]. There is information from many works, which indicated that clay mineral and their modified products i.e. porous clay, organo-modified clay, and acid treated clay are recognized as potential adsorbents. This is because of the ability itself of clay mineral that can exchange interlayer cations for charged organic cations in solution [22-25]. In addition, they also reported that the N_2 and CO_2 adsorption of organo-montmorillonite increased after treatment with organic cations. Researchers attempted to increase adsorptive capacity of clay mineral with using acid treatment. Acid treatment of clay minerals (by using mainly HCl or H_2SO_4 solutions) is chemical treatment of the clays to modify structural, textural and/or acidic properties, which influence the resulting properties of raw material such as acidity, surface area and adsorption capacity as well [22, 24, 26-27]. The octahedral ions are leached out, resulting in improving the surface area and gases adsorption capacity of the clay after acid treatment. Then the aim of this work was to enhance surface area, mechanical properties and also adsorption capacity of polyHIPE foam by using three types of organoclay as inorganic filler for poly(DVB)polyHIPE porous foam, including hybrid organic-inorganic porous clay heterostructure (HPCH) derived from organo-bentonite which prepared through surfactant-directed assembly of tetraethoxysilane (TEOS)/methyltetraethoxysilane (MTS) into galleries of clay mineral, organo-modified bentonite (MOD) treated with quaternary alkyl ammonium cation by ion exchange reaction, and acid treated organo-modified bentonite (AC-MOD), which treated with acid solution then treated with quaternary alkyl ammonium cation by ion exchange reaction. In order to study the effect of type of organoclay on overall properties of poly(DVB)polyHIPE porous foam.

6.3 Experimental

6.3.1 Materials

Divinylbenzene (DVB; Merck) was used as monomer to produce polyHIPE materials. Surfactant used in the study was sorbitant monooleate (Span80; S80), purchased from Sigma-Aldrich Chemical. Initiator and stabilizer used in the experiments were potassium persulfate ($K_2S_2O_8$, purity $\geq 98\%$ (RT), Fluka Chemie) and calcium chloride ($CaCl_2$, purity $\geq 97\%$ (KT), Fluka Chemie) respectively. Toluene (T) was employed as a porogenic solvent. Na-bentonite (BTN) was supplied by Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43 mmol/100g of clay.

In this study, The HPCH was prepared in our laboratory. The procedure for synthesis and characterization has been described by Prakobna *et al.* (2006) [28]. In addition, in order to obtain acid-activated organo-modified bentonite (AC-MOD), bentonite, which is clay mineral was modified by acid treatment with 3 N HCl solutions and treated with quaternary alkyl ammonium cations by ion exchange reaction. The structural characteristics of MOD and AC-MOD were studied using FT-IR, XRD and XRF. Three types organoclay was prepared from the following procedure.

- 1) Hybrid organic-inorganic Porous clay heterostructures (HPCH) Na-Bentonite (BTN) (Mac-Gel[®] GRADE SAC) was converted in to quaternary ammonium cations form by ion exchanged with cetyltrimethylammonium bromide (CTAB). Hybrid organic-inorganic porous clay heterostructures (HPCH) derived from Na-Bentonite were obtained by the surfactant-directed assembly of mesostructured silica within clay layers. The reaction carried out in the presence of intragallery surfactant templates (cetyltrimethylammonium ion and dedecylamine).

2) Organo-modified bentonite (MOD) derived from Na-Bentonite (BTN) (Mac-Gel[®] GRADE SAC): To increase d-spacing of organo-modified bentonite, synthesized Na-Bentonite was ion exchanged with quaternary ammonium cations by using Methyl bis(soya amidoethyl)-2-hydroxyethyl quaternary ammonium methyl sulfate (DOAM) as surfactant.

3) Acid treated organo-modified bentonite (AC-MOD) derived from Na-Bentonite (BTN) (Mac-Gel[®] GRADE SAC): BTN was modified by acid treatment with 3 N HCl solutions at 110°C for 3 h. The clay/acid ratio used in the study was 2% wt/wt. After treatment, the clay was separated and washed with distilled water several times and dries until constant weight was obtained and grind then treated with quaternary alkyl ammonium cations by ion exchange reaction. To increase d-spacing of acid treated bentonite, synthesized Na-bentonite was ion exchanged with quaternary ammonium cations by using Methyl bis(soya amidoethyl)-2-hydroxyethyl quaternary ammonium methyl sulfate (DOAM) as surfactant. The structural characteristics of organoclay (both MOD and AC-MOD) were studied using FT-IR, XRD and XRF.

6.3.2 Methods and Characterizations

6.3.2.1 *Preparation of poly(DVB)polyHIPE filled with organoclay*

Poly(DVB)PolyHIPE materials were prepared by using high internal phase emulsion. In the present work, poly(DVB)polyHIPE foam was fabricated and with using three types of organoclay including HPCH, MOD, and AC-MOD as filler. The continuous phase (10 vol% of total volume) of the emulsion consisted of DVB, toluene (monomer: porogen; 1:1 ratio by volume), surfactant and organoclay (0, 1, 3, 5 and 10 wt% relative to monomer). The aqueous phase, which contained water (90 ml), K₂S₂O₈ (0.2 g) as initiator and electrolyte; CaCl₂ (1.0 g). After all the water has been added, the emulsion was further stirred for 20 min and placed in a glass bottle. Emulsions were capped and put in a water bath at 60°C for 24 h. After polymerization, the cellular materials were removed from the glass

bottles and washed by Soxhlet extraction for 6 h with 2-propanol. Then the cellular materials were returned to vacuum oven to dry at 60°C until a constant weight was obtained.

6.3.2.2 Characterization of organo-modified clay (MOD) and Acid-treated organo-modified clay (AC-MOD)

X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organo-modified clay (MOD), and acid-treated clay (AC-MOD) and to investigate the crystal structure of nanocomposites. X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K α radiation operated at 40 kV and 30 mA. The powder samples were observed on the 2 θ range of 1.8-20 degree with scan speed 2 degree/min and scan step 0.02 degree.

Fourier Transform Infrared Spectroscopy (FT-IR)

The incorporation of organic group into silicate network by ion exchanged with quaternary ammonium cations was investigated by using FTIR. The FT-IR spectra of MOD and AC-MOD were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm $^{-1}$ with 32 scans at a resolution of 2 cm $^{-1}$. KBr pellet technique was applied in the preparation of powder samples.

X-ray Fluorescence (XRF)

Chemical compositions of MOD and AC-MOD were obtained using Oxford Model ED2000 X-ray tube with silver as a filter, operate at voltage 35 kV.

6.3.2.3 Characterization of Poly(DVB)PolyHIPE Nanocomposites Foam

Surface Area Analyzer (SAA)

N₂ 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. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

Thermogravimetric Analysis (TGA)

All PolyHIPE were determined by thermogravimetric analysis (TGA) using a Perkin-Elmer Pyris Diamond TG-DTA instrument under N₂ flow of 100 ml/min. The heating process was conducted from 30-800°C at a rate 10°C/min. The degradation temperature was determined at a weight loss 50% from the weight loss vs. temperature curve.

Differential Scanning Calorimetry (DSC)

The glass transition temperature of polyHIPE foam was determined using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 250°C and cooled down at a rate of 10°C/min under a N₂ atmosphere with a flow rate of 10 ml/min. The sample was then reheated to 250°C at the same rate.

Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL/JSM 5200 Model to observe surface morphology of poly(DVB)polyHIPE. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

Transmission Electron Microscope (TEM)

Transmission electron microscopy was also used in this study to observe the morphology of the poly(DVB)polyHIPE nanocomposites foam. TEM micrographs were taken on a Tecnai G2 Sphera electron microscope with an accelerating voltage of 80 kV to observe the pore structure and secondary pore in the cell wall of poly(DVB)polyHIPE. Micrographs were recorded at magnifications of 80000 \times and 150000 \times magnification. TEM samples were prepared by embedding polyHIPE nanocomposites foam in a support resin and sectioning on an ultra-thin microtome. The thin sections were supported on 300 mesh copper grids.

Universal Testing Machine (LLOYD)

A Lloyd Universal Testing Machine was used to measure the mechanical properties of all samples in compression mode, according to ASTM D822. Test specimens in a cylinder shape 2.54 cm in diameter \times 2.54 cm in length 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.

Adsorption of carbon dioxide (CO₂)

Adsorption of CO₂ was carried at room temperature using gas adsorption unit, which was made in laboratory of Department of Chemical Technology, Faculty of science, Chulalongkorn University. Samples were cut into small pieces weigh about 1–2 g and outgases at 100 °C prior to measurement. The samples were loaded into sample tube 2 \times 25 cm. CO₂ 3 mL/min and He 17 mL/min were flowed through the sample at room temperature. The amount of CO₂ gas adsorbed by the polyHIPE foam was determined by gas chromatography, column used Shimadzu 2014, and the detector was FID type using Helium (He) as the carrier gas.

6.4 Results and Discussion

6.4.1 Characterization of Organo-modified clay (MOD) and Acid-treated organo-modified clay (AC-MOD)

For HPCH, the characterization results are not shown in this paper because this organoclay was done already in our laboratory. All of results were described by Prakobna *et al.* (2006) [28]. However, the effect of acid treatment on the structural of clay was studied using XRF and BET. An important structural change of clay was observed for treated and untreated Na-bentonite with acid solution. Table 6.1 shows the chemical compositions of clay treated and untreated with acid treatment. Through acid treatment, the Si/(Al+Mg+Fe+Ti) molar ratios of the clay were changed from 4.96 to 10.06. This is because of the ability of acid treatment, the octahedral cations are leached out in the following order: Al>Fe>Mg>Ti, resulted in an increasing acid sites and specific surface area of clay treated with acid solution from 31.35 m²/g to 86.72 m²/g compared to BTN. This situation was found in many literatures, which reported that the chemical composition and surface properties of raw clay materials were changed after acid treatment [22, 27].

Generally, clay mineral is hydrophilic in nature and will separate from organic phase of polyHIPE. Therefore, modification of clay is necessary to increase its hydrophobicity and make it more compatibility with polyHIPE system. This research used DOAM of 1.5CEC as a surfactant for modifying the clay mineral. The modification of Na-bentonite with quaternary ammonium cations (surfactant) was prepared for both BTN and acid treated BTN. Clay mineral with ion exchanged with quaternary ammonium cations was denoted as MOD whereas clay mineral with acid treatment and ion exchanged with quaternary ammonium cations was denoted as AC-MOD. The presence of surfactant in clay was evidenced by FTIR and XRD results. FTIR spectra of organoclay (both MOD and AC-MOD; Figure 6.1b and 6.1c) shows similar pattern, which stretching vibration of the unsaturated ketone, and the asymmetric and symmetric stretching vibrations of alkanes occurred around 1700, and 2900 cm⁻¹, respectively, which are characteristics peaks of the surfactant templates. Therefore, from FTIR spectra, it was indicated that modification of BTN

with surfactant (DOAM) was successfully achieved for both MOD and AC-MOD. Moreover, a corresponding XRD pattern shows the presence of the (001) reflection peak. As seen from Figure 6.2a, the d_{001} peak of pristine Na-bentonite clay at $2\theta = 7.19^\circ$ corresponds to basal spacing of 1.544 nm. It can be observed for AC-MOD and MOD (Figure 6.2b and 6.2c), the d_{001} peaks were appeared at lower angle than that of neat bentonite, corresponding to an increase on the basal spacing of the organoclay, which the value for MOD and AC-MOD were 3.906 and 4.042 nm, respectively. This result revealed that the interlayer distance of bentonite was expanded by ion exchange reaction with quaternary ammonium cations and further increased for AC-MOD when proton (H^+) was added.

6.4.2 Characterization of Poly(DVB)PolyHIPE Filled with Organoclay

In order to study the effect of type and loading of organoclay, three type of organoclay including HPCH, MOD and AC-MOD with various wt% (i.e. 1, 3, 5, 10 wt%) were used as a inorganic reinforcement of poly(DVB)polyHIPE foam. All polyHIPE system exhibited the similar behavior, indicated that all HPCH, MOD and AC-MOD can be used as filler for polyHIPE foam leading to improve the overall properties of the resulting polyHIPE materials i.e., surface area, thermal behavior and mechanical properties and adsorption of CO_2 .

6.4.2.1 *Phase Morphology*

Phase morphology of poly(DVB)polyHIPE foam filled with various type of organoclay has been investigated. Figure 6.3 represents to phase morphology of poly(DVB)polyHIPE foam filled with three type of organo-bentonite including HPCH, MOD, AC-MOD and pure polyHIPE foam as reference (see Figure 6.3a). All samples exhibited same morphology appearance which showed three dimensional open cellular porous structures. This result indicated that organoclay can incorporate to polyHIPE matrix without effecting highly porous structure and pore interconnectivity as well [21]. However, phase morphology of poly(DVB)polyHIPE foam filled with various weight percents of organoclay (organoclay; 1, 3, 5, 10 wt%) has been investigated. From SEM micrographs with high magnification (see Figure 6.4), it clearly shows that the roughness of the wall surface seem to increase when

organoclay was added into polyHIPE matrix and was further increased with the increase in organoclay content. This could be due to the incorporation of organoclay into the continuous phase of polyHIPE foams, which can be supported with the elemental analysis results which showed that the Si peak was observed when the organoclay can incorporate into the continuous phase of polyHIPE system (see Figure 6.5).

6.4.2.2 Surface Area

Surface area of poly(DVB)polyHIPE nanocomposite foams prepared by using three different types of organoclay i.e. HPCH, MOD and AC-MOD was determined. A typical N₂ adsorption-desorption isotherm for poly(DVB)polyHIPE nanocomposites foam is displayed in Figure 6.6. The shape of N₂ adsorption-desorption isotherms of all poly(DVB)polyHIPE foams filled with organoclay was found to be relatively similar, shows a hysteresis loop which may belongs to a type IV BET isotherm according to the BDDT classification. The BET specific surface areas of the obtained poly(DVB)polyHIPE nanocomposites foam were between 132–270 m²/g. Figure 6.7 and Table 6.2 show surface properties of poly(DVB)polyHIPE foam with HPCH, MOD and AC-MOD with various weight percentage. All polyHIPE foams filled with HPCH, MOD and AC-MOD revealed the similar behavior, the surface areas for the series of poly(DVB)polyHIPE nanocomposite foams were found to increase with wt% of organoclay (0 to 10 wt%). The changes in surface areas with different organoclay content can be explained using SEM micrographs of the obtained poly(DVB)polyHIPE nanocomposite foams with high magnification (see Figure 6.4), indicated that the roughness of the wall surface of the resulting polyHIPE foam increased as organoclay content increased from 0-10 wt% resulting in improving the surface area of the obtained polyHIPE foam. Additionally, the increasing in surface area of resulting polyHIPE nanocomposite foams could be due to ability itself of organoclay that can adsorb gas molecules into the layered silicates. For polyHIPE foam filled with MOD and AC-MOD, increasing in the surface area attributed to the increasing of d-spacing of MOD via the ion exchange reaction with quaternary ammonium cations whereas polyHIPE foam filled with HPCH may be due to the inherent characteristics of

HPCH which exhibited open-framework of silica with uniform pore diameter in the clay galleries. At 10 wt% of organoclay in the polyHIPE system, surface area increased by 98%, 66% and 103% for poly(DVB)polyHIPE filled with HPCH, MOD and AC-MOD, respectively. Furthermore, to study the effect of acid treatment of organoclay on the surface properties, poly(DVB)polyHIPE foam filled with MOD was used as comparable with poly(DVB)polyHIPE foam filled with AC-MOD. In the series of poly(DVB)polyHIPE foam filled with AC-MOD, the surface area showed the higher value than polyHIPE foam filled with MOD. After acid treatment, the octahedral cations were removed from the clay layer resulting in the increasing of acidity and porosity of AC-MOD. Thus the high surface area of poly(DVB)polyHIPE foam filled with AC-MOD was attributed to the high surface properties and porosity of AC-MOD.

6.4.2.3 Thermal Properties

The effect of organoclay on thermal behavior of poly(DVB)polyHIPE nanocomposite foam was investigated. TG analysis of poly(DVB)polyHIPE nanocomposite foam, prepared with various wt% of organoclay (0 to 10 wt%), was carried out. The decomposition temperature (T_d) of all polyHIPE foam filled with organoclay including HPCH, MOD and AC-MOD is listed in Table 6.2. As compared with pure poly(DVB)polyHIPE foam, the poly(DVB)polyHIPE nanocomposite foam have higher decomposition temperature (T_d) and also slightly increased with the organoclay content. The reason should be attributed to the incorporation of organoclay nanoparticles into poly(DVB)polyHIPE matrix resulting in the formation of a high-performance carbonaceous-silicate char builds up on the polyHIPEs surface. Organoclay also offers a stabilizing effect against decomposition, so T_d was shifted towards higher temperature.

The glass transition temperature (T_g) of the polyHIPE foam with and without organoclay was investigated by using DSC with the temperature range between 30-250°C and heating rate of 10°Cmin⁻¹. It was found that no glass transition temperature can be detected from both neat polyHIPE foams and poly(DVB)polyHIPE nanocomposite foam (see Figure 6.8). Because, in preparation of poly(DVB)polyHIPE foam, DVB was used as a crosslinking agent as well as a

monomer in the organic phase. So, the high degree of crosslinking of DVB was obtained lead to absence of a glass transition temperature (T_g). These observations were consistent with the results from many works (Shim *et al.*, 2004; Mener *et al.*, 2006 and Jin *et al.*, 2007), which indicated that no glass transition temperature (T_g) was detected due to the high degree of DVB lead to high degree of crosslinking [29-31].

6.4.2.4 Mechanical Properties

Mechanical properties of poly(DVB)polyHIPE nanocomposite foams, prepared from three types of organoclay at various clay content were studied using LLOYD Universal Testing Machine. Mechanical properties of the all samples including compressive stress and Young's modulus are shown in Figure 6.9, Figure 6.10, and Table 6.3. In the presence of organoclay, both compressive stress and Young's modulus exhibited higher value when compared to the neat poly(DVB)polyHIPE foam. In all systems, the maximum improvement was occurred at 5 wt%. Compressive stress was found to increase up to 115%, 114% and 48% for poly(DVB)polyHIPE foam filled with HPCH, MOD and AC-MOD, respectively whereas Young's modulus increased by up to 214%, 205% and 52%, respectively. The high aspect ratio and large surface area of organoclay leading to provide the better stress transfer between polyHIPE matrix and organoclay, which contributed to the improvement of mechanical performance [32-33]. This situation could be obtained by the addition of organoclay with good dispersion into the continuous phase of poly(DVB)polyHIPE nanocomposite foams. TEM micrographs of poly(DVB)polyHIPE nanocomposites foam in Figure 6.11 show both intercalated and exfoliated clay platelets dispersed through out polyHIPE matrix. However, TEM micrograph with high magnification ($\times 150000$), indicated that the well dispersion of organoclay through polyHIPE matrix can be resulted in the better stress transfer between two phases. In addition, this result was in accordance to results from elemental analysis, indicated that organoclay particles were uniformly dispersed in the continuous of polyHIPE foam (see Figure 6.12). Nevertheless, the mechanical properties of obtained polyHIPE foam were found to reduce when weight percent of organoclay up to 10 wt% because of the agglomeration of organoclay, acting as weak point in the continuous of polyHIPE matrix. This assumption was supported by

evidence from EDX images (see Figure 6.12d), which clearly show that large agglomerates of organoclay particle at 10 wt% loading, which may act as stress concentrator in the poly(DVB)polyHIPE foams.

6.4.2.5 Adsorption of CO₂

The adsorption values of CO₂ by poly(DVB)polyHIPE nanocomposite foams and pristine poly(DVB)polyHIPE foam were investigated. Figure 6.13 shows the adsorption capacity of poly(DVB)polyHIPE foam both filled and unfilled with organoclay. In this study, three type of organoclay including HPCH, MOD and AC-MOD with 10 wt% was applied. The amount of CO₂ adsorbed with poly(DVB)polyHIPE nanocomposites foam was 0.0046 mole/g, 0.0048 mole/g and 0.0067 mole/g for MOD, HPCH and AC-MOD, respectively. Comparing to the neat poly(DVB)polyHIPE foam (gas adsorption of CO₂ = 0.00295 mol/g), all sample of poly(DVB)polyHIPE foam filled with organoclay exhibited higher adsorption capacity of CO₂ because the ability of organoclay could adsorb gas molecules in the interlayer structure. Moreover, this result also showed that the highest adsorption capacity was obtained when AC-MOD was used as filler in poly(DVB)polyHIPE nanocomposite foams. Organoclay with acid treatment can improve the gas adsorption of CO₂ due to increasing the surface area, acidity and changes of the chemical composition in the interlayer, compared with poly(DVB)polyHIPE foam filled with MOD.

6.5 Conclusions

Poly(DVB)polyHIPE foam can offer an alternative use as adsorbent in gas adsorption process. In order to improve properties and also adsorption capacity of polyHIPE foam, three types of organoclay derived from Na-bentonite i.e. HPCH, MOD and AC-MOD could be utilized as inorganic reinforcement. The results showed poly(DVB)polyHIPE nanocomposites foam created a good adsorbent for CO₂ gas adsorption and exhibited the higher CO₂ adsorption capacity, compared with neat poly(DVB)polyHIPE foam. This could be due to the presence of organoclay into continuous phase of polyHIPE matrix, which organoclay itself can be adsorbed such gas into interlayer lead to improve the adsorption of CO₂ gas of the obtained

polyHIPE foam. By modification clay material with quaternary ammonium cations via ion exchange reaction, formation of pore structure into galleries of clay mineral and acid treatment, the CO₂ gas adsorption of poly(DVB)polyHIPE nanocomposites foam was increased in the following order: neat poly(DVB)polyHIPE foam < poly(DVB)polyHIPE foam filled with MOD ≤ poly(DVB)polyHIPE foam filled with HPCH < poly(DVB)polyHIPE foam filled with AC-MOD. Moreover, the effectiveness of organoclay leads to improve overall properties of the obtained polyHIPE foam including surface area, decomposition temperature and mechanical properties

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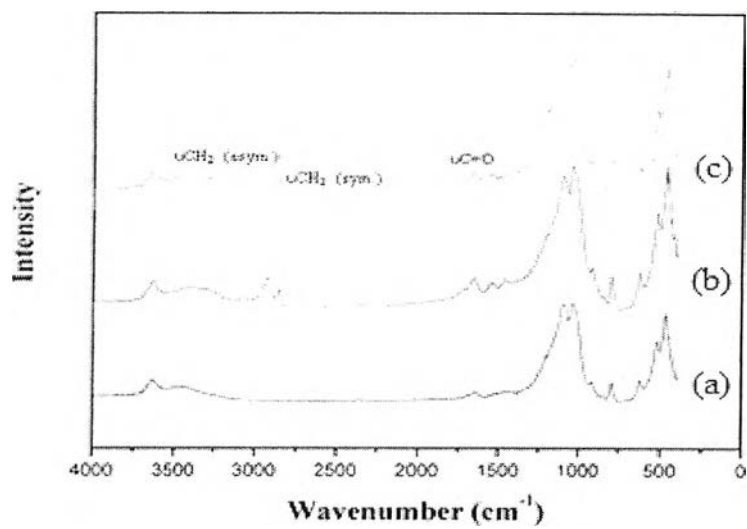


Figure 6.1 FTIR spectra of (a) Bentonite (BTN), (b) Organo-modified clay (MOD), and (c) Acid treated organo-modified clay (AC-MOD).

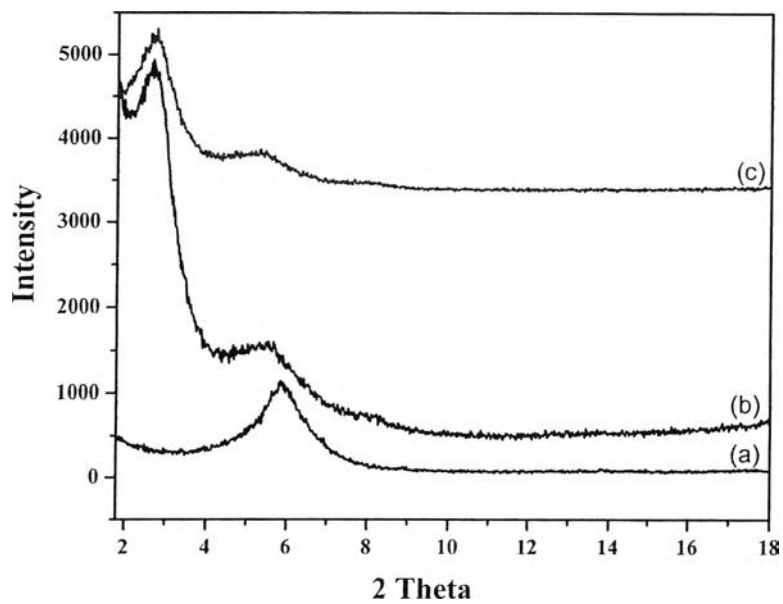


Figure 6.2 XRD pattern of (a) Bentonite (BTN), (b) Organo-modified clay (MOD), and (c) Acid treated organo-modified clay (AC-MOD).

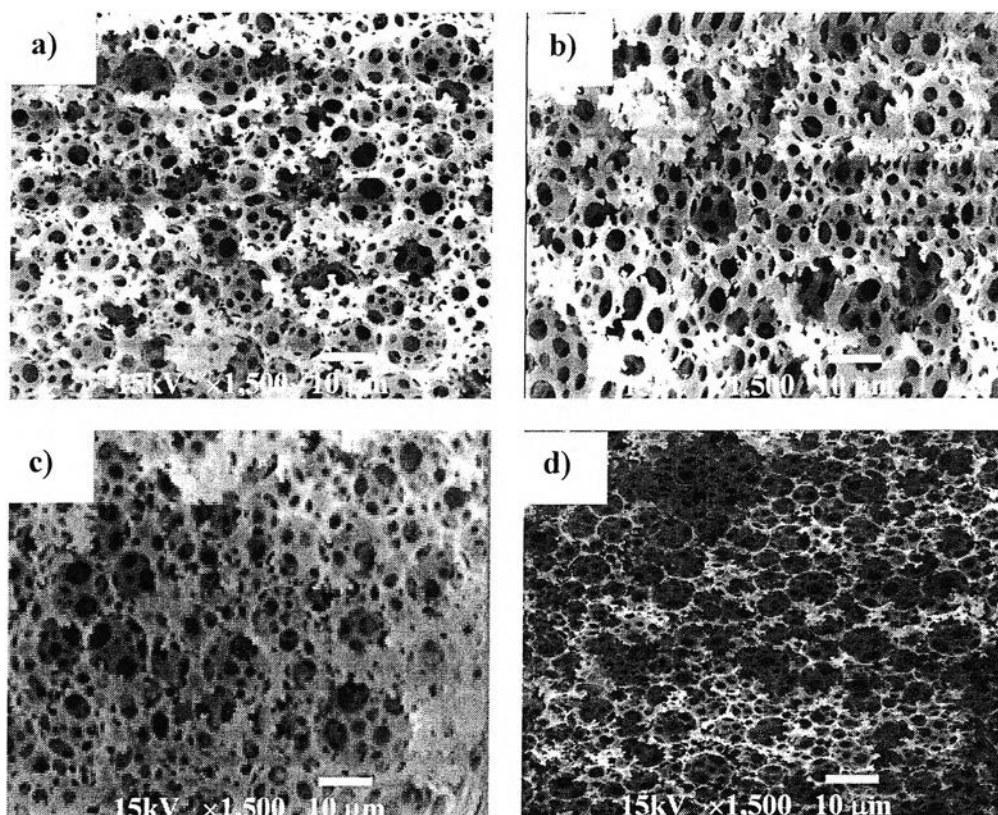


Figure 6.3 SEM micrographs of poly(DVB)polyHIPE nanocomposites foam filled with organoclay (1 wt%): a) without organoclay; b) HPCH; c) MOD; d) AC-MOD.

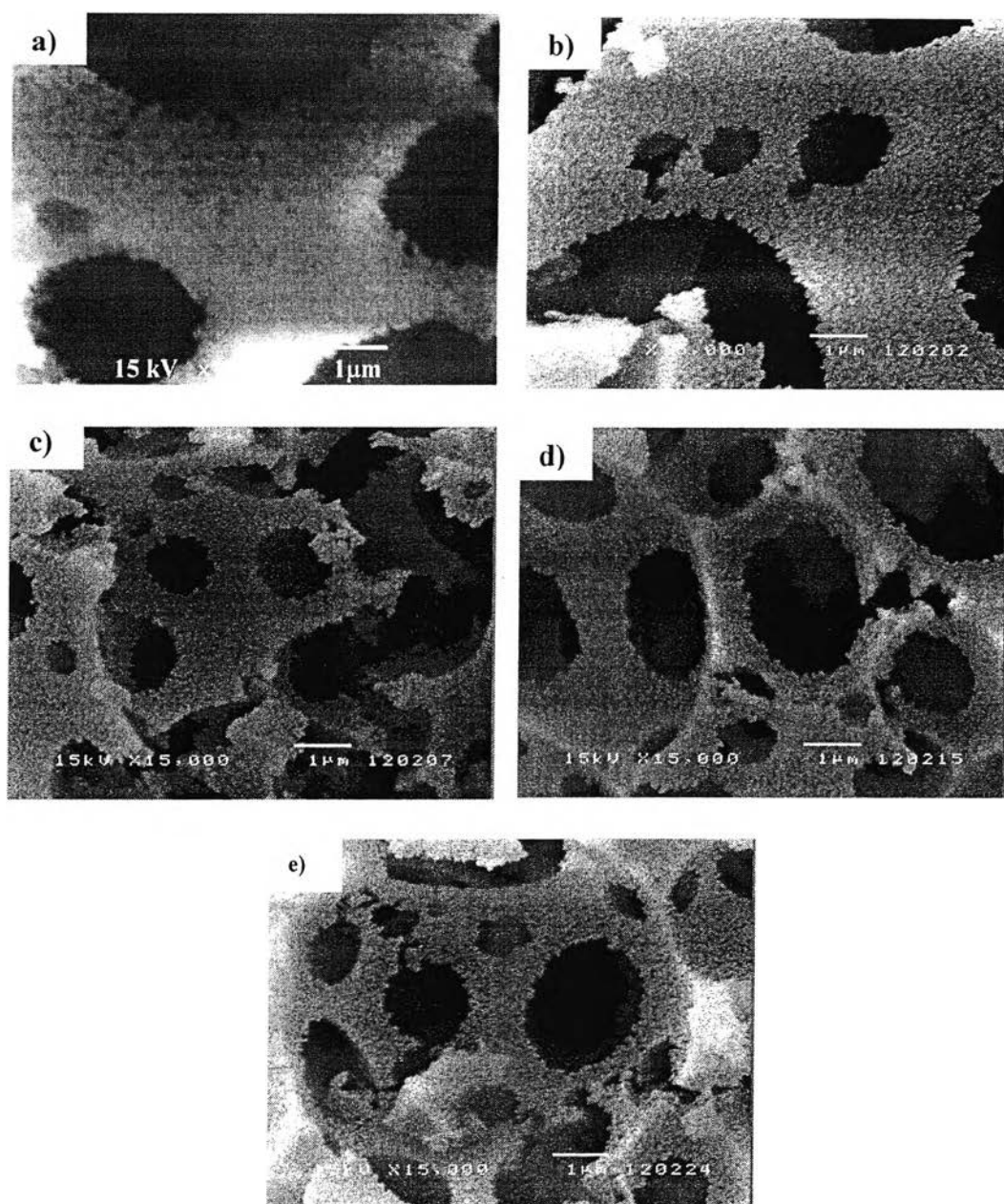


Figure 6.4 Scanning electron micrographs of poly(DVB)polyHIPE filled with various weight percentage of organoclay at high magnification ($\times 15000$): a) reference (0 wt% organoclay), b) 1 wt% organoclay; c) 3 wt% organoclay; d) 5 wt% organoclay; and e) 10 wt% organoclay.

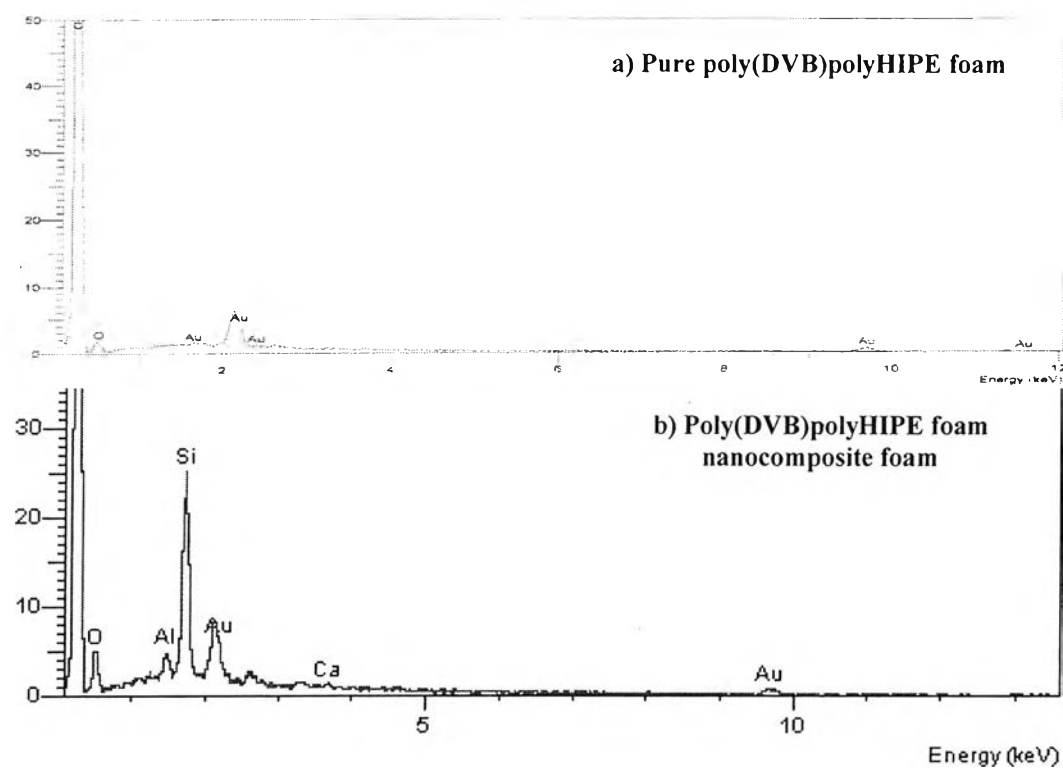


Figure 6.5 EDX spectra of poly(DVB)polyHIPE: a) Pure poly(DVB)polyHIPE foam and b) Poly(DVB)polyHIPE foam nanocomposites foam.

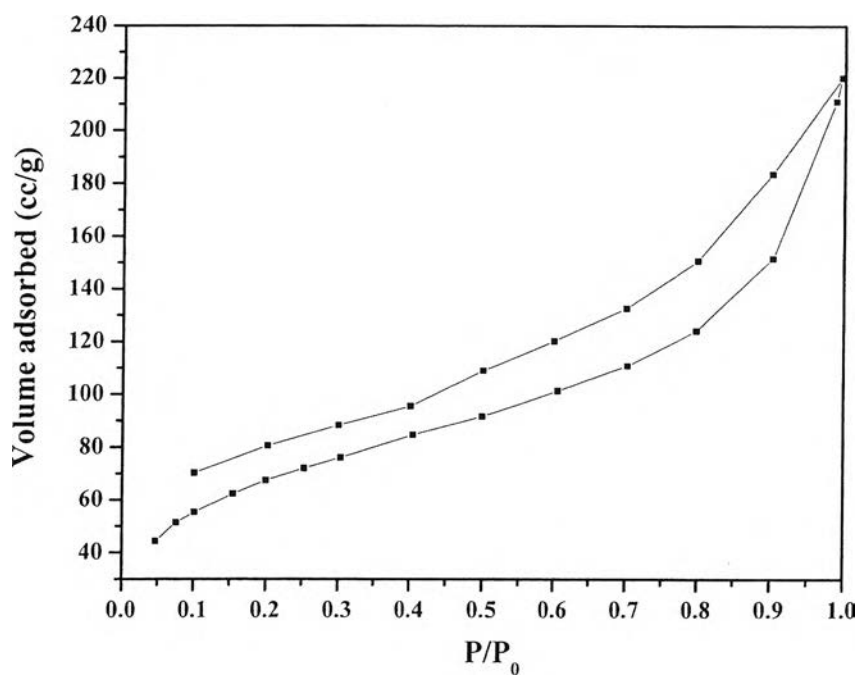


Figure 6.6 Typical example of N_2 adsorption-desorption isotherm for poly(DVB)polyHIPE nanocomposites foam.

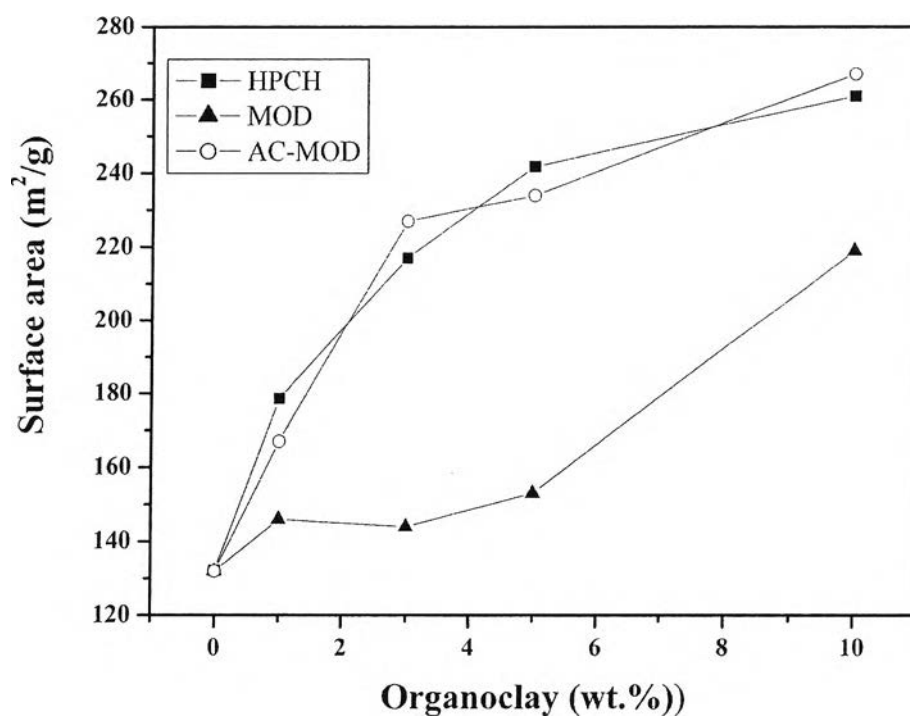


Figure 6.7 Surface area of poly(DVB)polyHIPE nanocomposites foam filled with three type of organoclay i.e. HPCH, MOD, and AC-MOD.

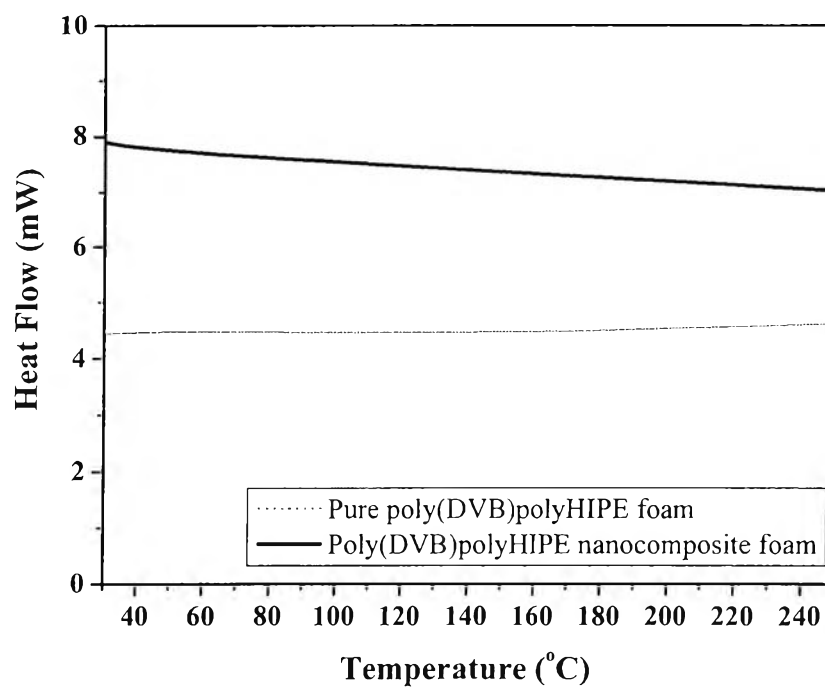


Figure 6.8 DSC thermograms of the poly(DVB)polyHIPE foam with and with out organoclay. Dashed line denotes the thermogram of neat poly(DVB)polyHIPE foam in the absence of organoclay and solid line denotes the thermogram of poly(DVB)polyHIPE nanocomposites foam.

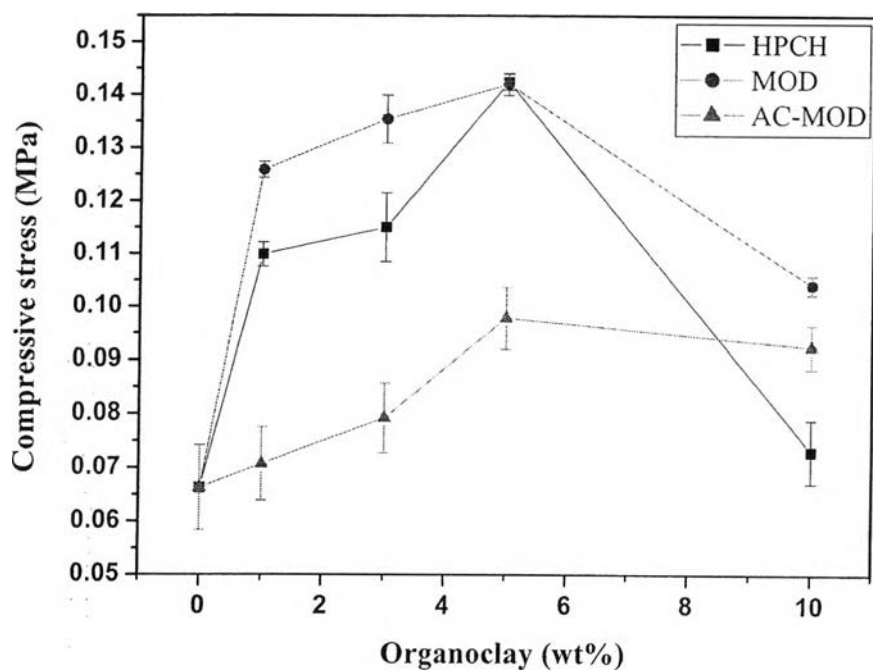


Figure 6.9 Compressive stress of poly(DVB)polyHIPE nanocomposites foam filled with three type of organoclay i.e. HPCH, MOD, and AC-MOD.

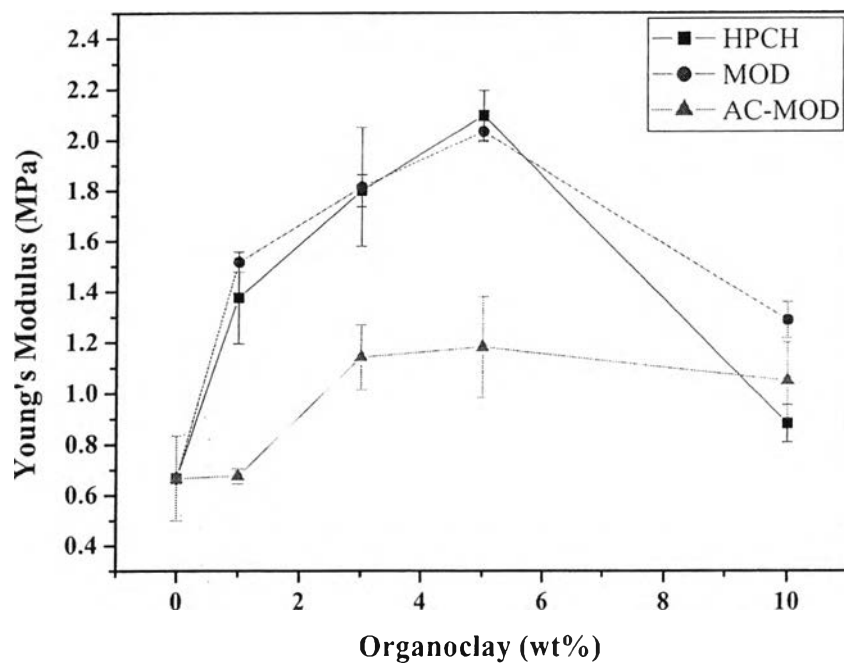


Figure 6.10 Young's modulus of poly(DVB)polyHIPE nanocomposites foam filled with three type of organoclay i.e. HPCH, MOD, and AC-MOD.

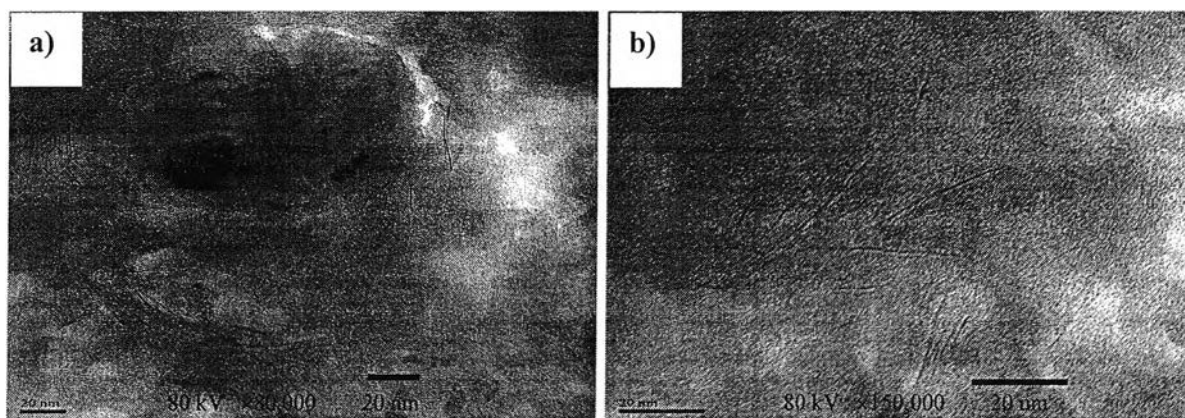


Figure 6.11 High-resolution TEM images of poly(DVB)polyHIPE nanocomposites foam.

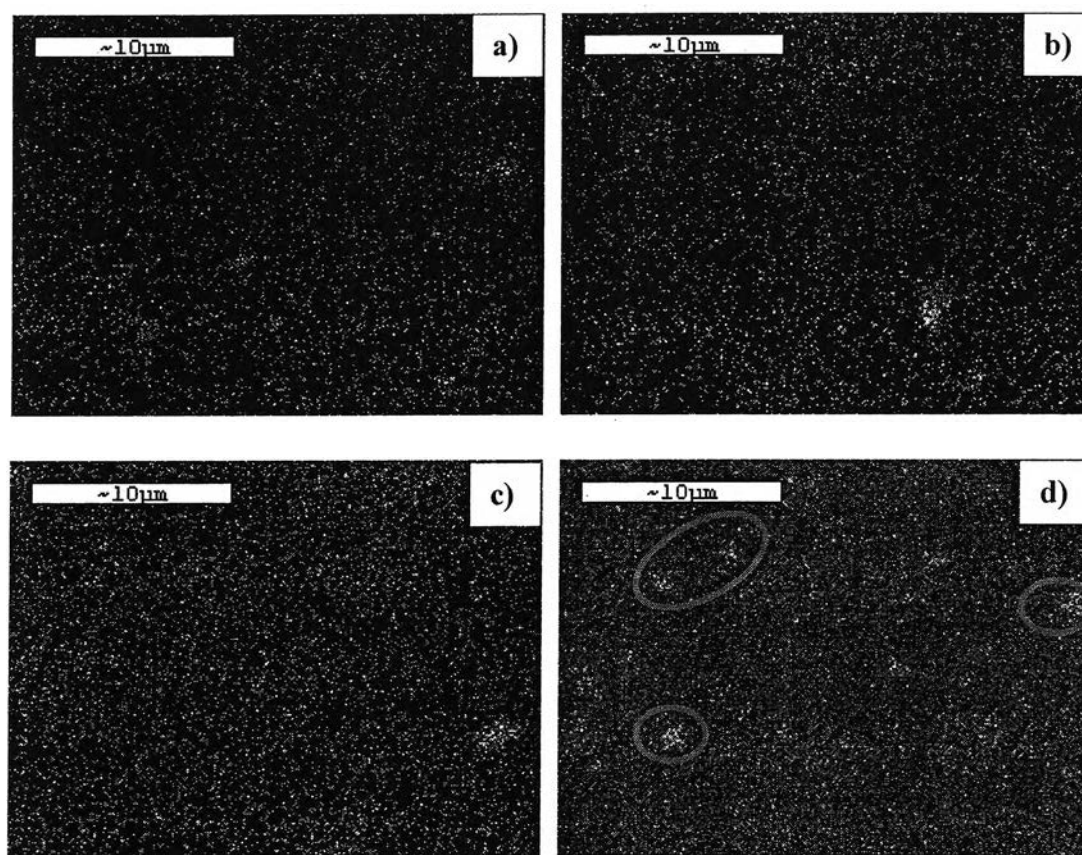


Figure 6.12 Spectra Si mapping of scanning electron micrographs of poly(DVB)polyHIPE: a) 1 wt% organoclay; b) 3 wt% organoclay; c) 5 wt% organoclay; and d) 10 wt% organoclay.

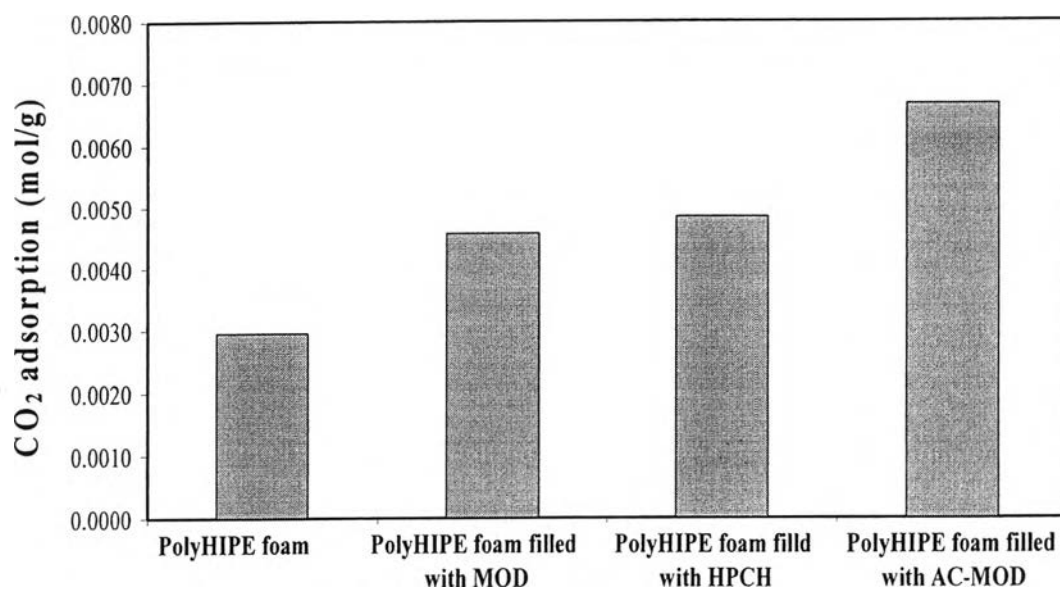


Figure 6.13 CO₂ gas adsorption of poly(DVB)polyHIPE nanocomposites foam filled with three type of organoclay i.e., HPCH, MOD and AC-MOD.

Table 6.1 Chemical compositions of clay from XRF i.e., untreated and treated with acid treatment. (Oct: cations in octahedral position: Al, Mg, Fe and Ti).

Sample	SiO₂ %	Al₂O₃ %	MgO %	Fe₂O₃ %	TiO₂ %	Si/Oct molar
Untreated BTN	77.78	9.94	1.02	2.20	0.37	4.96
Treated BTN	87.96	5.64	0.42	0.99	0.40	10.06

Table 6.2 Surface areas and decomposition temperature (T_d) of poly(DVB)polyHIPE filled with different type of organoclay i.e. HPCH, MOD and AC-MOD.

Poly(DVB)polyHIPE with S80 system	Surface area (m²/g)	T_d (°C)	Poly(DVB)polyHIPE with S80 system	Surface area (m²/g)	T_d (°C)	Poly(DVB)polyHIPE with S80system	Surface area (m²/g)	T_d (°C)
0 wt% HPCH	132	438.05	0 wt% MOD	132	438.05	0 wt% AC-MOD	132	427.40
1 wt% HPCH	179	441.70	1 wt% MOD	146	440.70	1 wt% AC-MOD	167	429.50
3 wt% HPCH	217	443.50	3 wt% MOD	144	442.90	3 wt% AC-MOD	227	430.90
5 wt% HPCH	242	445.88	5 wt% MOD	153	445.60	5 wt% AC-MOD	234	432.00
10 wt% HPCH	261	451.65	10 wt% MOD	219	448.73	10 wt% AC-MOD	269	434.90

Table 6.3 Mechanical properties of poly(DVB)polyHIPE filled with different type of organoclay i.e. HPCH, MOD and AC-MOD.

Poly(DVB)poly HIPE with S80 system	Compressive stress (MPa)	Young's Modulus (MPa)	Poly(DVB)polyHIPE with S80 system	Compressive stress (MPa)	Young's Modulus (MPa)	Poly(DVB)polyHIPE with S80system	Compressive stress (MPa)	Young's Modulus (MPa)
0 wt% HPCH	0.0663 ± 0.0079	0.6674 ± 0.1675	0 wt% MOD	0.0663 ± 0.0079	0.6674 ± 0.1675	0 wt% AC-MOD	0.0663 ± 0.0079	0.6674 ± 0.1675
1 wt% HPCH	0.1099 ± 0.0023	1.3765 ± 0.1812	1 wt% MOD	0.1259 ± 0.0015	1.5172 ± 0.0393	1 wt% AC-MOD	0.0707 ± 0.0068	0.6764 ± 0.0296
3 wt% HPCH	0.1150 ± 0.0065	1.8002 ± 0.0632	3 wt% MOD	0.1354 ± 0.0045	1.8153 ± 0.2356	3 wt% AC-MOD	0.0792 ± 0.0065	1.1419 ± 0.1273
5 wt% HPCH	0.1424 ± 0.0015	2.0979 ± 0.0979	5 wt% MOD	0.1420 ± 0.0210	2.0346 ± 0.0411	5 wt% AC-MOD	0.0978 ± 0.0059	1.1821 ± 0.1979
10 wt% HPCH	0.0730 ± 0.0059	0.8825 ± 0.0727	10 wt% MOD	0.1041 ± 0.0018	1.2875 ± 0.0710	10 wt% AC-MOD	0.0924 ± 0.0041	1.0494 ± 0.1504