

CHAPTER IV
MODIFICATION OF POROUS CLAY HETEROSTRUCTURES (PCHs) AND
HYBRID ORGANIC-INORGANIC PCHs (HPCHs) FOR
ETHYLENE ENTRAPPING SYSTEM

4.1 ABSTRACT

Porous clay heterostructures (PCHs) and hybrid organic-inorganic PCHs (HPCHs) were prepared through surfactant-directed assembly of tetraethoxysilane (TEOS) and TEOS/methyltetraethoxysilane (MTS) into the galleries of Na-bentonite clay, respectively. The reaction involves hydrolysis and condensation of TEOS and MTS in the presence of intragallery surfactant templates (cetyltrimethylammonium ion and dedecylamine). Before the synthesis, pH of the bentonite clay was adjusted to 4 conditions including pH 9, 7, 5 and 3. To investigate the effect of pH on the formation of porous structures, the products were characterized by N₂ adsorption-desorption, XRD, SEM, TEM and FTIR techniques. The results reveal that PCHs have surface areas of 501-668 m²/g, an average pore diameter in the supermicropore to small mesopore range of 3.01-3.85 nm, and a pore volume of 0.43-0.64 cc/g, while HPCHs have a result of 469-582 m²/g, 3.19-3.88 nm, and 0.33-0.49 cc/g, respectively. New applications of the PCHs and HPCHs materials are expected in active packaging for ethylene entrapping system. The ethylene adsorption capacity of these porous clays was investigated using gas chromatography. The results reveal that the enhancement of the hydrophobicity on HPCHs play an important role in ethylene adsorption.

keywords : porous clay heterostructures, bentonite, ethylene adsorption.

4.2 INTRODUCTION

The synthesis of porous materials has attracted much interest due to they offer many advantages as adsorbents, gas separation devices or gas-storage materials [1]. Recently, the discovery of a new class of porous materials known as porous clay heterostructures (PCHs) has been proposed [2]. This porous material is prepared by surfactant-directed assembly of silica in the two dimensional interlayer spacing of

clays [3-7]. The PCHs materials reveal important properties such as exhibiting high surface areas with uniform and specific pore sizes in the rarely observed supermicropore to small mesopore region [7]. In the synthesis of PCHs, layered clays are first intercalated with cationic surfactants. Neutral amine co-surfactant molecules are then intercalated along with silica species which leads to the polymerization of siloxane network surrounding the surfactant micelles in the clay galleries. Then, an open-framework of silica is formed in the galleries after surfactant removal [8]. Moreover, the chemical properties of these mesoporous materials are modified via the incorporation of organic components. The important way to prepare hybrid organic-inorganic porous clay heterostructures (HPCHs) is a cocondensation reaction of a tetraalkoxysilane and an organoalkoxysilane (also called “one-pot” synthesis) [9-11]. From this viewpoint, these porous materials could find application in many fields.

Both PCHs and HPCHs materials are capable of utilizing as inorganic particles in polymer nanocomposites owing to their structures still remain as clay galleries. Generally, polymer nanocomposites are defined as the combination of a polymer matrix resin and inorganic particles (usually 10 wt% or less), which have at least one dimensional (i.e. length, width, or thickness) in the nanometer size range, acting as a nano-reinforcement [12-16]. Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhance mechanical, thermal and barrier properties of the virgin polymer [14].

In the present work, the modification of porous clay heterostructures (PCHs) and hybrid organic-inorganic PCHs (HPCHs) has been focused. Before the synthesis of PCHs and HPCHs, pH of Na-bentonite was adjusted to be 9, 7, 5 and 3. After that, the effect of pH on the formation of porous structure was investigated. Moreover, we try to find a new application of the PCHs and HPCHs materials for ethylene scavenger in food packaging owing to the presence of uniform and specific porous structures providing high surface area. In addition, they can be improved ethylene adsorption capacity by the incorporation of methyl groups enhancing hydrophobic surface in the HPCHs materials. We focus on the ethylene scavenging system because ethylene has been recognized as a plant hormone controlling ripening and senescence in fruits and vegetables. If ethylene produced by fresh fruits accumulates

in the packaging, it accelerates the ripening and makes the fruit excessively soft and mealy in very low concentration [17].

4.3 EXPERIMENTAL

Materials

Na-Bentonite (BTN), (Mac-Gel® GRADE SAC), was obtained from Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43 mmol/100g of clay.

Cetyltrimethylammonium [$C_{16}H_{33}N^+(CH_3)_3$] bromide (CTAB) was supplied by Fluka. Dodecylamine, $C_{12}H_{27}N$, (98% purified) was supplied by Aldrich. Tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_4$ and Methyltriethyl orthosilicate (MTS), $CH_3Si(OC_2H_5)_3$, were purchased from Fluka. Methanol (CH_3OH) was supplied by Lab Scan and Hydrochloric acid (HCl) was supplied by Carlo Erba.

Purification and pH Adjustment of Bentonite Clay

Na-bentonite (BTN) was pulverized and sieve through 325 mesh. Four 10-g of the passing part were purified by centrifugation and then washed with distilled water several times until pH value was near 9. After that, centrifugation was applied. Again, the same amount of distilled water was added, and then the pH of three samples was adjusted to 3, 5, and 7 by using dilute HCl solution. This procedure was repeated for three days to equilibrate the pH of each sample. The samples were air-dried overnight and again pulverized in a mortar.

Formation of Porous Clay Heterostructures (PCHs)

Each 3 g of pH-adjusted bentonite was converted into a quaternary ammonium form by ion exchange with 50 ml of 0.1 M aqueous cetyltrimethylammonium bromide and stirred at 50 °C for 24 h. After the reaction time, the solid was filtered out, washed with a mixture of methanol and water and then air-dried. The obtained organoclay was stirred in dodecylamine for 30 min at 50°C. In addition, TEOS (at molar ratio of organoclay:dodecylamine: TEOS was 1:20:150) was added and the resulting suspension was stirred for further 4 h at room

temperature. The solid was separated from solution again by filtration and air-dried overnight at room temperature to form the as-synthesized PCHs. The surfactant was removed from the as-synthesized PCHs by solvent extraction using methanol/HCl solution. Typically, 1 g of the as-synthesized PCHs material has been added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The solid was subsequently filtrated out and washed with a mixture of methanol and water and dried at 70°C under vacuum for 2 hr. The obtained PCHs are named PCH-n (n denotes the pH value of pH-adjusted bentonite clay).

Modification of Hybrid Organic-Inorganic Porous Clay Heterostructures (HPCHs)

The pH-adjusted bentonite was converted into a quaternary ammonium exchange form to obtained organoclay and reacted with dodecylamine according to PCHs formation procedure previously. Then a mixture of TEOS and MTS in a mole fraction of 1:1 was added and stirred for further 12 h at 35 °C. The obtained as-synthesized organic modified PCHs (HPCHs) were collected by centrifugation and air-dried overnight at room temperature. The surfactant was removed from the as-synthesized HPCHs by solvent extraction using methanol/HCl solution with the same procedure as described in PCHs formation. The obtained HPCHs are named HPCH-n (n denotes the pH value of pH-adjusted bentonite clay).

Physical Measurements

Powder 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 2θ range of 2-20 degree with a scan speed of 2 degree/min and a scan step of 0.02 degree.

N₂ adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Powder samples were degassed at 150°C during 12 h under vacuum 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.

Scanning electron microscopy was performed on JSM-6400 Model. The specimens were coated with gold under vacuum to make them electrically conductive.

Transmission electron microscopy was performed on JEOL JEM-2100 model and an accelerating voltage of 150 kV. TEM samples were prepared by embedding the powder in resin and sectioning on a ultramicrotome.

Gas chromatography (Agilent Technologies 6890 Network GC system) and HP-PLOT Q column: 30 m x 0.32 mm ID with flame ionization detector was utilized to examine ethylene adsorption capacity of the porous clays. Helium gas was used as carrier gas and the initial temperature for injection step was 150 °C. Ethylene adsorption was measured by placing each product in a jar (0.6 l), then sealing with a screw-cap lid. Ethylene was injected into a jar to give a specific concentration of 500 ppm. Ethylene concentration in the jar was measured periodically about once an hour. The ethylene adsorption was calculated by taking the difference between the amount of ethylene added and the amount of remaining in the headspace.

Chemical Analysis

FT-IR spectra of organoclays, PCHs, and HPCHs 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. The incorporation of organic group into silicate network is investigated by using FTIR technique.

4.4 RESULTS AND DISCUSSION

Characterization of Bentonite, pH-Adjusted Bentonite and Organo Bentonite

Na-Bentonite (BTN) which has a cationic exchange capacity (CEC) of 43.5 mmol/100g clay was adjusted pH to 9, 7 and 5. A corresponding XRD pattern of the samples are shown in Figure 4.1, the basal spacing of BTN is 1.49 nm (Figure 4.1(a)). For pH-adjusted BTN (Figure 4.1(b)-(e)), the reflection peak are observed at marginally lower angle than the pristine BTN and the basal spacing are 1.50, 1.51, 1.53 and 1.51 nm when the pH of samples was adjusted to 9, 7, 5 and 3, respectively. This result reveals that the interlayer distance of BTN is slightly expanded when more amount of proton (H^+) is added.

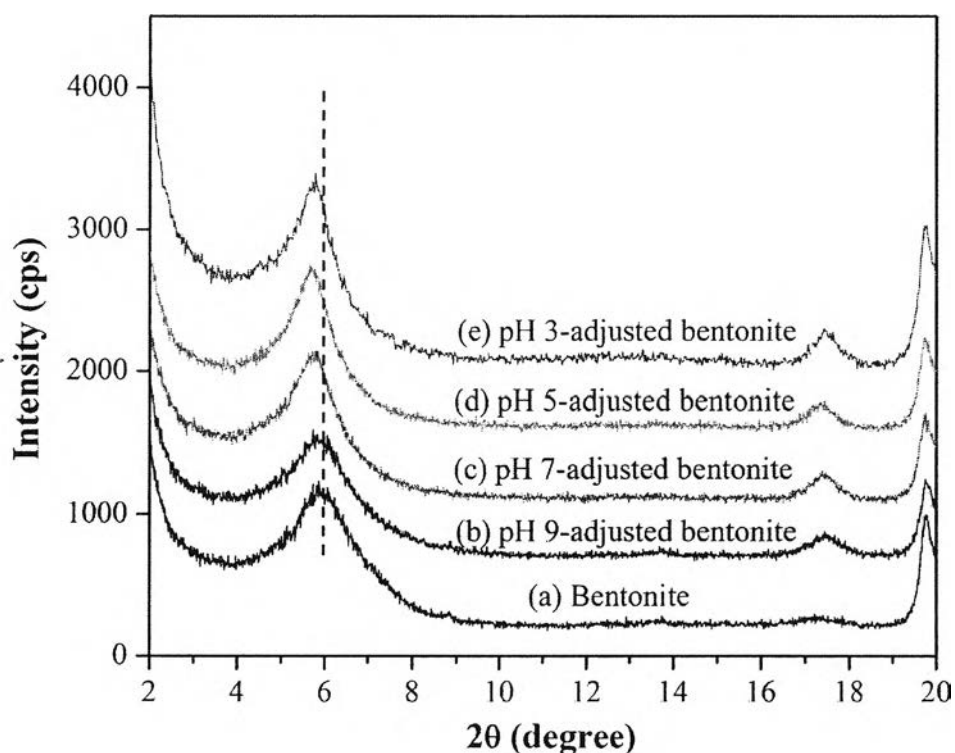


Figure 4.1 XRD patterns of BTN and pH-adjusted BTN.

When each pH-adjusted BTN was treated with cetyltrimethylammonium bromide (CTAB), the peak of starting clay at $2\theta = 5.94^\circ$ ($d = 1.49$ nm) disappeared. Moreover, two strong new peak are observed at lower angle (Fig. 4.2 (b)-(e)) as a consequence of the successful intercalation of cationic surfactant in the interlayer of BTN, resulting in the increasing of distance between clay layers. The results are shown in Tables 4.1 and 4.2.

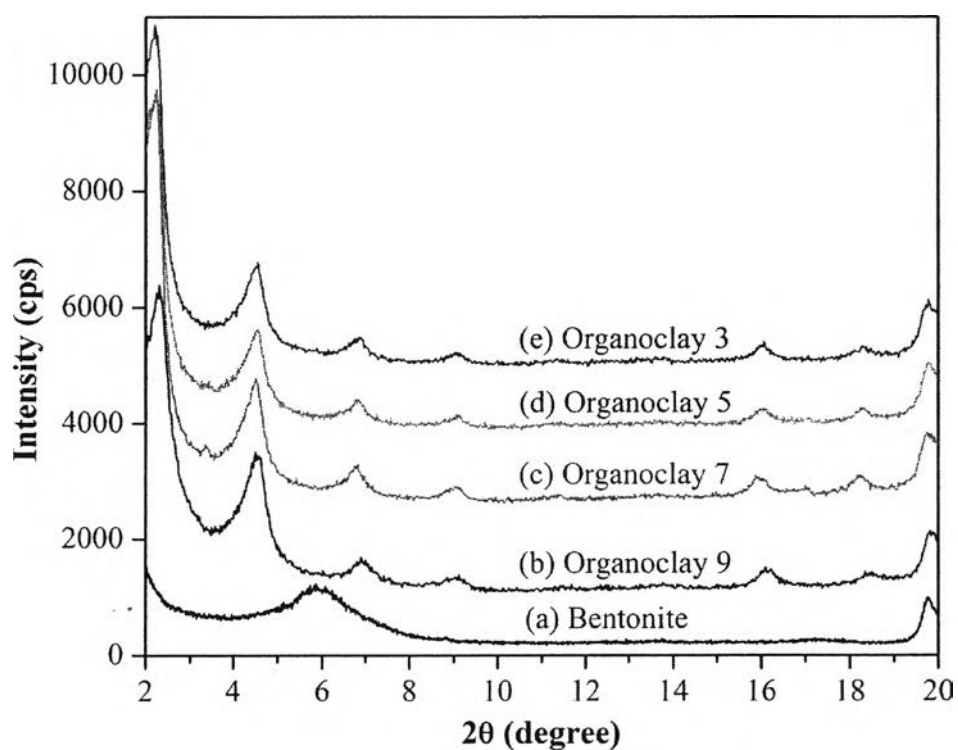


Figure 4.2 XRD patterns of BTN and organo BTN.

Table 4.1 Comparison of the basal spacing of BTN and pH-adjusted BTN

Sample	2 θ (degree)	d-value (nm)
BTN	5.94	1.49
pH 9-adjusted BTN	5.89	1.50
pH 7-adjusted BTN	5.86	1.51
pH 5-adjusted BTN	5.76	1.53
pH 3-adjusted BTN	5.86	1.51

Table 4.2 Comparison of the basal spacing of BTN and organoclay of BTN

Sample	2 θ (degree)	d-value (nm)
BTN	5.49	1.49
Organoclay 9	2.32	3.80
	4.62	1.91
Organoclay 7.	2.28	3.87
	4.56	1.94
Organoclay 5	2.26	3.91
	4.60	1.92
Organoclay 3	2.26	3.91
	3.91	1.92

Formation of Porous Clay Heterostructures (PCHs) and Hybrid Organic-Inorganic PCHs (HPCHs)

Before the synthesis of PCHs and HPCHs, pH of the bentonite was adjusted and equilibrated. After that, the clay galleries were first opened up by the intercalation of the surfactant cetyltrimethylammonium cation. Subsequently, neutral amine co-surfactant was then intercalated between clay layers to form micelle

templates. Then silica sources (TEOS and TEOS/MTS for PCHs and HPCHs, respectively) were introduced to polymerize surrounding the surfactant micelles in the galleries of clay. By solvent extraction method, the surfactant templates were removed from as-synthesized PCHs and HPCHs, resulting in the formation of porous structures.

After the intercalation of co-surfactant and silica sources, as-synthesize PCHs and HPCHs are obtained. XRD patterns of these samples are illustrated in Fig. 4.3. There is no obvious peak observed in the XRD patterns of these as-synthesized products. A possible reason due to disordered structure of silica framework which is formed in the galleries of clay shields a highly regular interstratification of the clay layers.

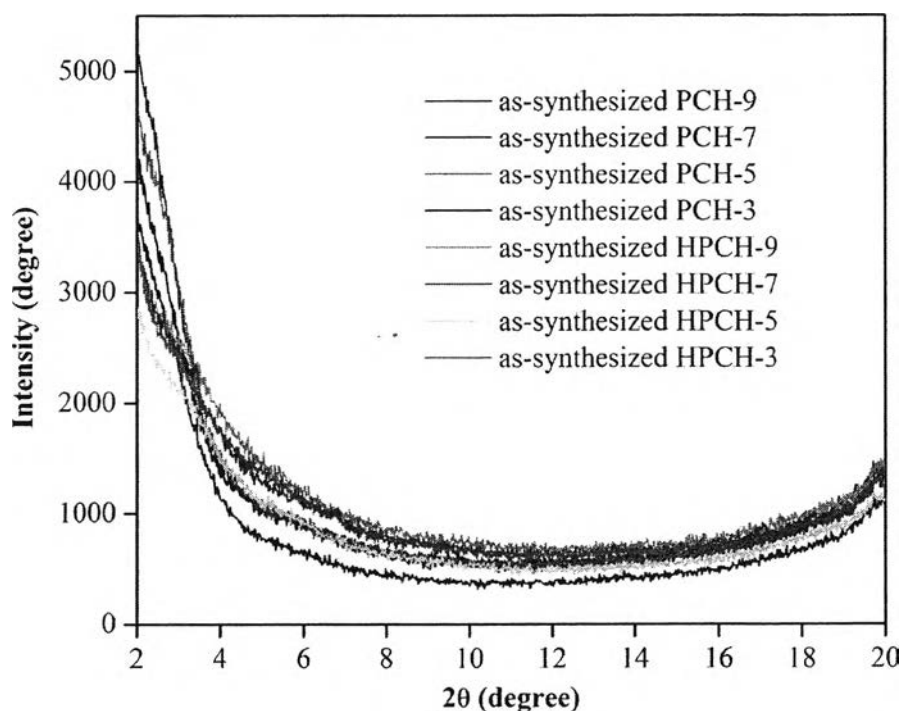
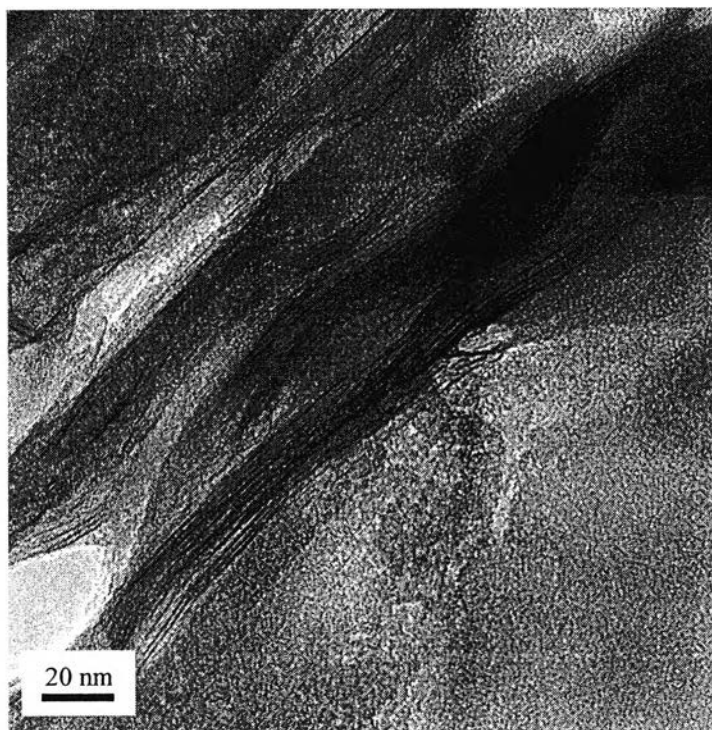
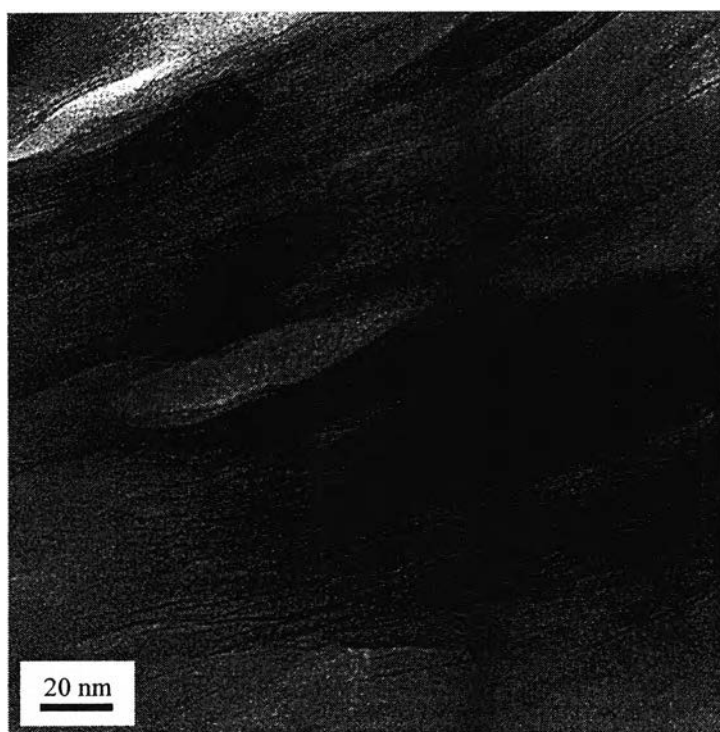


Figure 4.3 XRD patterns of as-synthesized PCHs and HPCHs.

However, the presence of the clay layers can be confirmed by TEM images of representatives of both PCHs and HPCHs (Fig. 4.4(a) and (b)). From the TEM images, the clay layers are discernible as solid dark lines and reveal aggregated domains of several layers. Although the clay layers are easily observed, pore structure in the galleries of clay is more difficult to notice due to the nature of these materials.



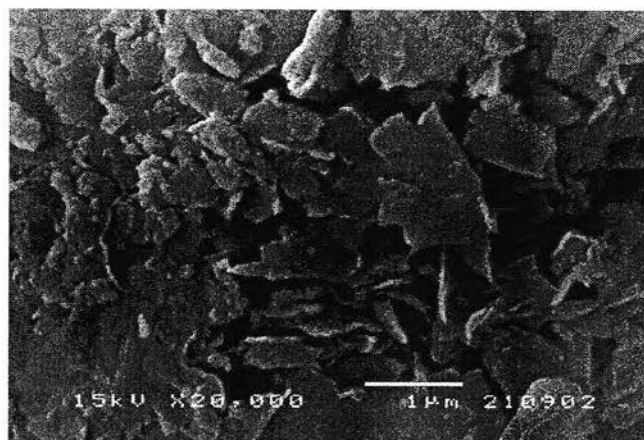
(a)



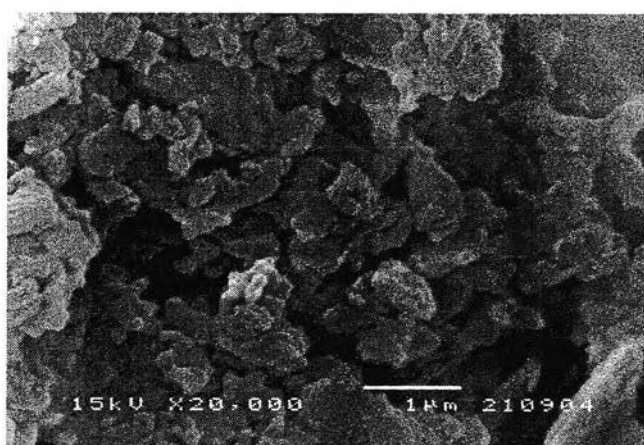
(b)

Figure 4.4 TEM images of (a) PCH-9 and (b) HPCH-9 .

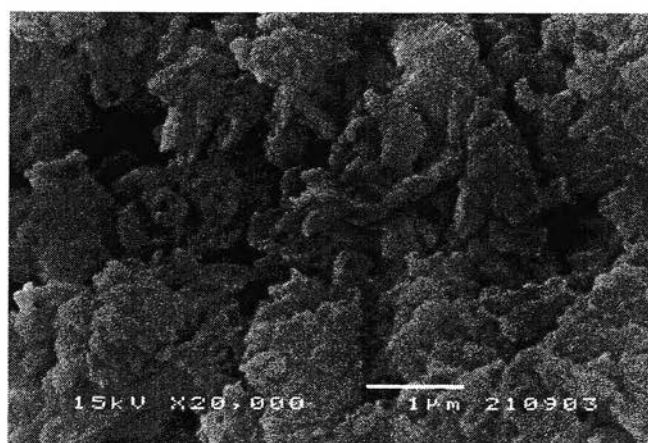
Furthermore, the BTN exhibit a layered or plate-like structure in SEM image (Fig. 4.5(a)). According to N₂ adsorption-desorption results in Fig. 4.6, 4.7 and Table 4.3. The isotherm of BTN shows a characteristic of non-porous solid indicating low adsorption amount of nitrogen and present a plateau exactly parallel to the pressure axis. Moreover, the BET surface area of BTN is 31 m²/g. After modification, the SEM images of PCH and HPCH (Fig. 4.5(b)-(c)) reveal a similar morphology to starting clay. Furthermore, the surface areas of PCHs and HPCHs increase significantly compared to those of pristine clay. The results show that PCHs and HPCHs have surface areas of 501-668 and 467-582 m²/g, average pore diameter in the supermicropore to small mesopore range of 3.01-3.85 and 3.19-3.88 nm and pore volume of 0.43-0.64 and 0.33-0.49 cc/g, respectively. The porous structures of PCHs and HPCHs are not affected by pH condition. All isotherms of PCHs and HPCHs are abruptly increase in nitrogen adsorption at low partial pressure and gradually increase to medium partial pressure (P/P₀:0.05-0.3), suggesting that these materials possess supermicropore to small mesopore region.



(a)



(b)



(c)

Figure 4.5 SEM images of (a) BTN, (b) PCH-9 and (c) HPCH-9.

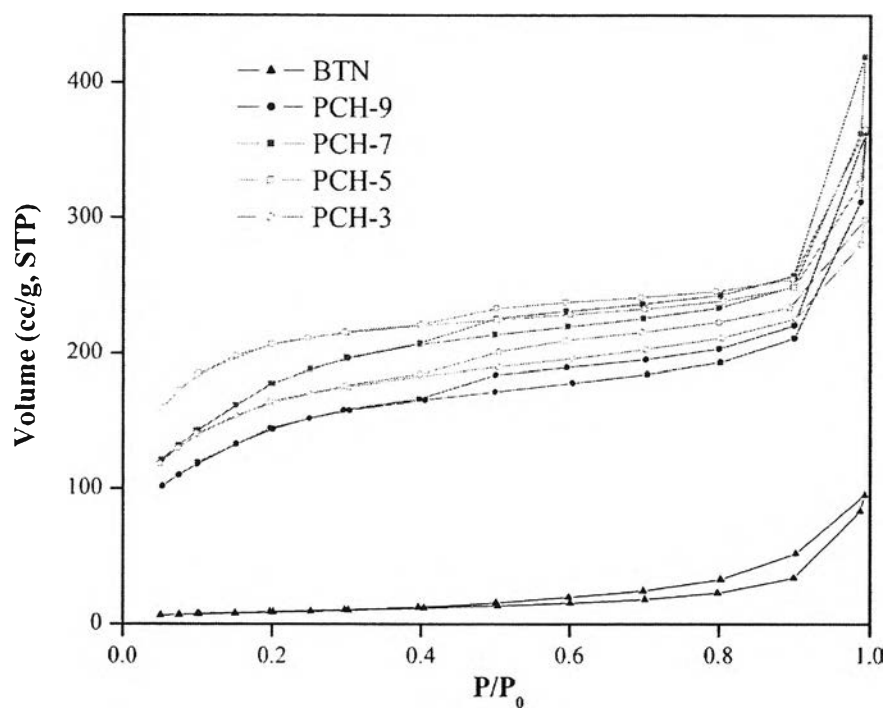


Figure 4.6 N_2 adsorption-desorption isotherms of BTN and PCHs.

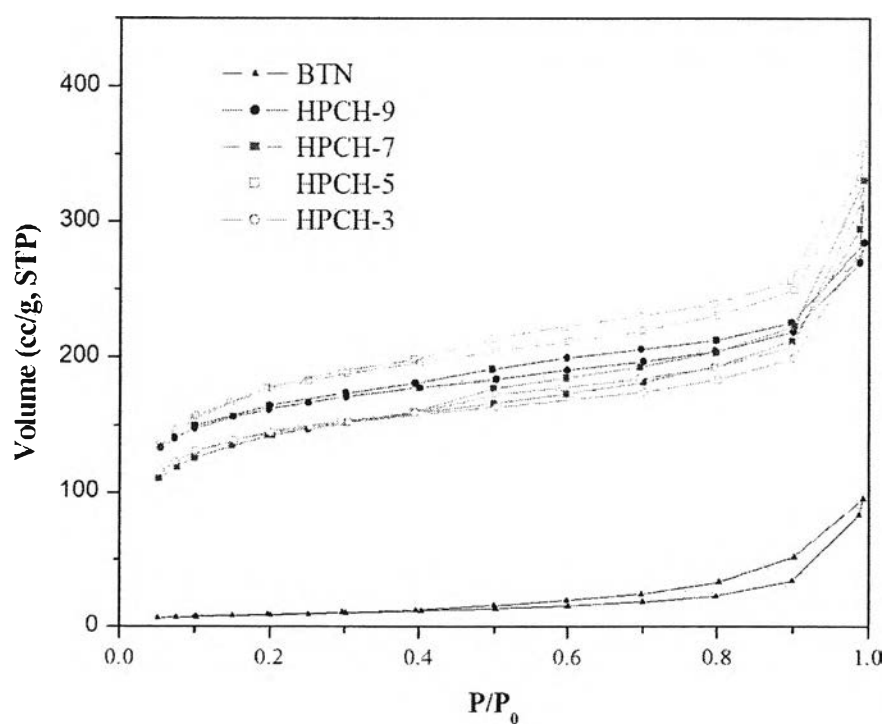


Figure 4.7 N_2 adsorption-desorption isotherms of BTN and HPCHs.

Table 4.3 Porosity characteristics of BTN, PCHs and HPCHs obtained from various pH-adjusted BTN.

Sample	Multipoint BET surface area (m ² /g)	Average pore diameter (nm)	BJH pore volume (cc/g)
Bentonite	31	16.45	0.15
PCH-9	501	3.85	0.54
PCH- 7	628	3.57	0.64
PCH -5	668	3.01	0.47
PCH- 3	549	3.16	0.43
HPCH-9	469	3.88	0.45
HPCH-7	524	3.19	0.33
HPCH -5	582	3.54	0.49
HPCH 3	467	3.68	0.41

The FTIR spectrum of BTN is given in Fig. 4.8(a). The broad peak around 3500 cm⁻¹ can be assigned to the stretching vibration of the silanol associated with the silica structure. The peak at 1000, 1100 and 800 cm⁻¹ can be assigned to the stretching vibration of the SiO₄ units, the asymmetric and symmetric stretching vibrations of the Si-O-Si linkage, respectively [14]. The presence of surfactant is evidenced by FTIR spectra of organoclay-9 (Fig. 4.8(b)) indicating the asymmetric and symmetric vibrations of methyl and methylene groups of cetyltrimethyl ammonium ion at 2920 and 2800 cm⁻¹, respectively. For clarity, only the spectrum of as-synthesized HPCH-9 (Fig. 4.8(c)), which has surfactant templates, and spectra of solvent-extracted HPCH-9 (Fig. 4.8(d)-(e)) are selected to confirm that removal of surfactant in as-synthesized HPCH-9 by solvent extraction in methanol and hydrochloric system is an effective method to eliminate the surfactant templates due to the absence of peak at 2920 and 2985 cm⁻¹ in solvent-extracted samples. The FTIR spectra of PCHs and HPCHs (Fig. 4.9(b)-(e) and 4.10(b)-(e), respectively) are different from starting BTN indicated by the absence of peak at 1000 cm⁻¹. So it

roughly infer that the structure of starting clay are changed after the modification. Moreover, the spectra of HPCHs ((Fig. 4.10(b)-(e)) evidenced that organic moiety is linked covalently to silica framework due to the presence of peak at 1275 cm^{-1} attributed to Si-C bond [11, 18].

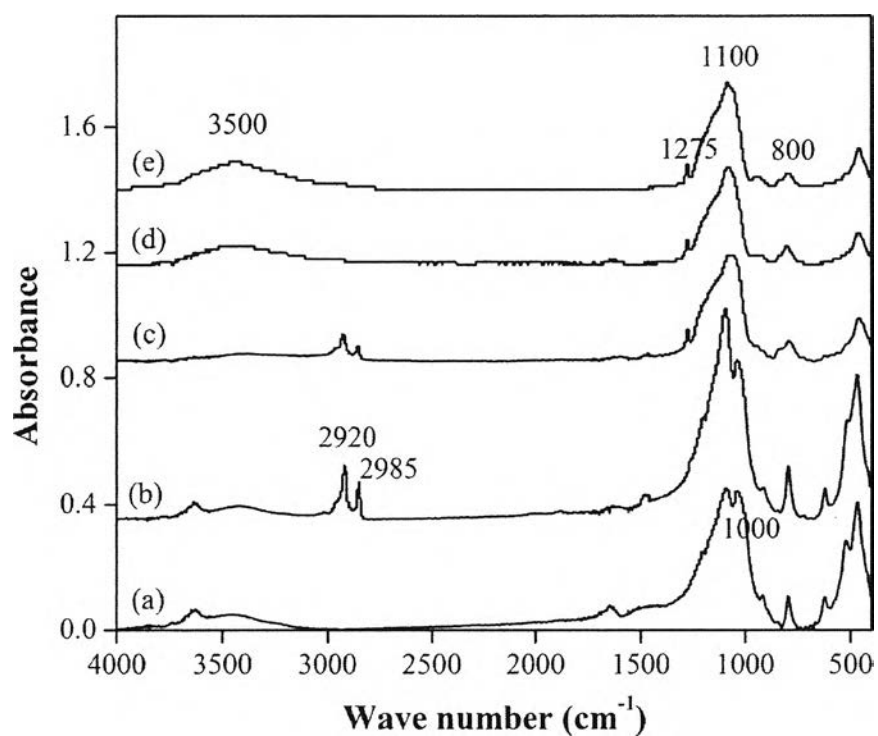


Figure 4.8 FTIR spectra of (a) BTN, (b) organoclay-9, (c) as-synthesized HPCH-9, (d) HPCH-9 before dried under vacuum, (e) HPCH-9 after dried under vacuum.

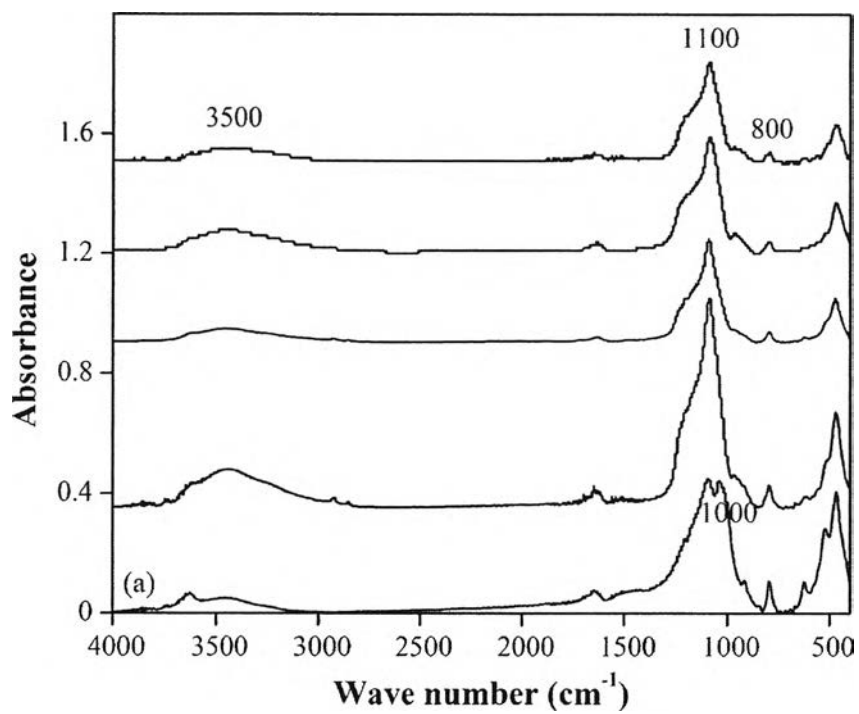


Figure 4.9 FTIR spectra of (a) BTN, (b) PCH-9, (c) PCH-7, (d) PCH-5 and (e) PCH-3.

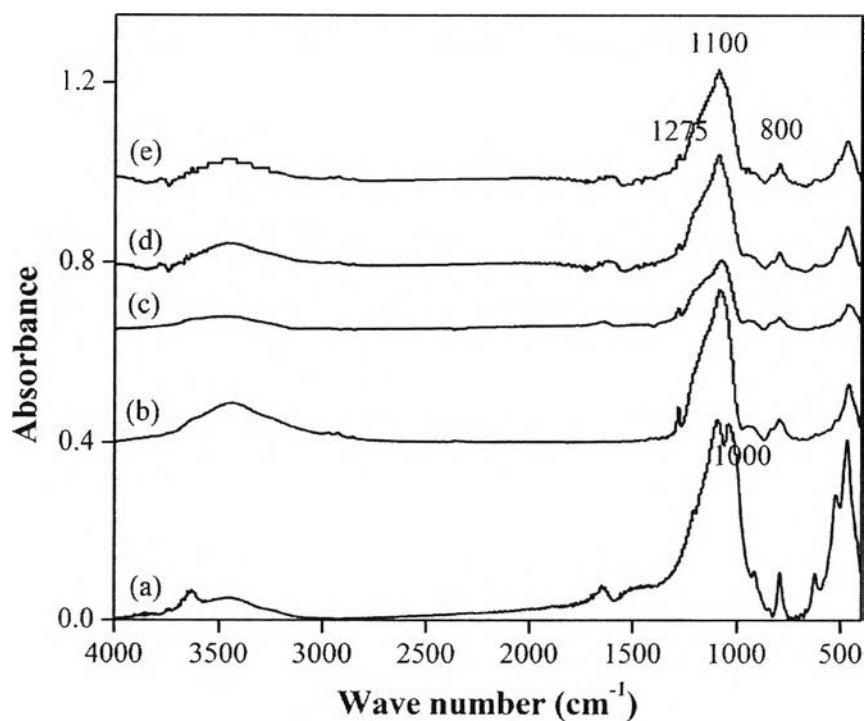


Figure 4.10 FTIR spectra of (a) BTN, (b) HPCH-9, (c) HPCH-7, (d) HPCH-5 and (e) HPCH-3.

Ethylene Adsorption

Adsorption behavior of ethylene gas within the PCHs and HPCHs materials was examined using gas chromatography. The PCHs and HPCHs are modified for utilize as ethylene scavenger in food packaging film due to the physical characteristics of these porous clays such as surface area, pore size and also chemical characteristic such as hydrophobicity on the surface. The samples must be heated before ethylene adsorption would occur to remove volatile molecules from the porous clays. Fig. 4.11 depicts the adsorption capacity of the PCHs and HPCHs. The amount of ethylene adsorption proportionally increased with time. Moreover, adsorption rates for these ethylene scavenger are fast at the beginning. The capacity of HPCHs prepared by the incorporation of methyl group on the porous structures is significantly better than PCHs. From the results presented in this work, it is clear that the enhancement of the hydrophobicity on HPCHs play an important role in ethylene adsorption. So it is possible to use these porous clays as ethylene scavenger.

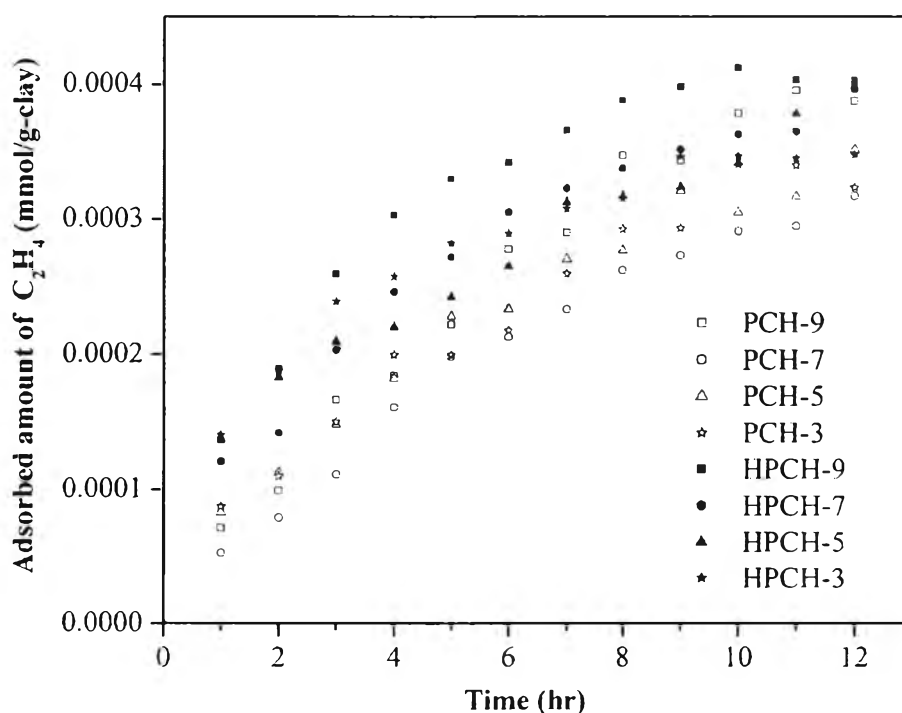


Figure 4.11 Ethylene adsorption capacity of various PCHs and HPCHs.

4.5 CONCLUSIONS

Porous clay heterostructures (PCHs) and hybrid organic-inorganic PCHs (HPCHs) derived from Na-bentonite clay have been synthesized by a surfactant directed assembly of silica species within the clay galleries. Before the modification, the pristine clay was adjusted pH to four conditions, including pH 9, 7, 5, and 3. HPCHs have been functionalized with the methyl group through co-condensation reaction to improve the hydrophobicity on the porous structures for finding a new application of these porous clays for ethylene scavenger films in active packaging. From the analysis of N₂ adsorption-desorption data, the results show that PCHs have surface areas of 501-668 m²/g, an average pore diameter in the supermicropore to small mesopore range of 3.01-3.85 nm, and a pore volume of 0.43-0.64 cc/g, while HPCHs have a result of 469-582 m²/g, 3.19-3.88 nm, and 0.33-0.49 cc/g, respectively. Moreover, the shape of the N₂ adsorption-desorption isotherms of these products are very similar which belong to a type IV BET isotherm, and also indicated that the framework pore sizes are in the supermicropore to small mesopore region. Furthermore, both PCHs and HPCHs reveal the possibility of finding a new application for utilize as ethylene scavenger. The results indicate that the ethylene adsorption capacity of HPCHs is significantly better than PCHs. From the results presented in this work, it is clear that the enhancement of the hydrophobicity on HPCHs play an important role in ethylene adsorption.

4.6 ACKNOWLEDGEMENTS

This work is funded by Thailand Research Fund (TRF). The authors would also thanks Polymer Processing and Polymer Nanomaterial Research Unit and Petroleum and Petrochemical Technology (PPT) Consortium for their partially funding.

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