

CHAPTER IV

SURFACE-MODIFIED POROUS CLAY HETEROSTRUCTURES (PCHs) FOR MAGNETIC PROPERTIES ENHANCEMENT

4.1 Abstract

Porous clay heterostructures (PCHs) provide a large specific area that can be modified by a functional group. In this work, a PCH surface was modified by Fe (Fe^{2+} and Fe^{3+}) from the ferric chloride hexahydrate and ferrous chloride tetrahydrate to obtain the magnetic PCH. The various Mn ion (Manganese (II) chloride tetrahydrate) contents were added into magnetic PCH to enhance the magnetic properties. To investigate the porous structures, PCH and Magnetic PCH were characterized by N_2 adsorption-desorption, XRD, SEM, TEM and FTIR techniques. The results reveal that magnetic PCH had surface areas lower than PCH. From SEM images and consistent EDX micrograph of Fe ion and Mn ion in PCH, the results showed that the incorporation of Fe ion and Mn ion in PCH was successful. The saturation magnetizations (M_s) of Magnetic PCHs were characterized by Vibration Sample Magnetometer (VSM). The results show that the saturation magnetization increases with higher the Mn concentrations.

keywords : Porous clay heterostructures (PCHs), saturation magnetization (M_s), Manganese

4.2 Introduction

Porous clay heterostructures (PCHs) are a new class of porous materials [1]. This porous material is prepared by surfactant-directed assembly of silica in the two dimensional interlayer spacing of clays [2-6]. 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 [6]. 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 [7]. From this viewpoint, the PCH surface area is higher than organoclay, making it suitable for easily modified by functional group and higher surface area for scavenging system. The previous work [8] showed the dramatically enhanced surface area of PCH compared to bentonite and successfully attached the surface of PCH with methyl group. These modified PCH exhibited the increasing of ethylene adsorption. Srithamaraj and co workers [9] involved the modification of PCH's surface by thiol group to enhance the conductive properties of these PCHs.

This work was focused on another point of view; to enhance the magnetic properties of PCH surface. The PCH surface was modified by Fe^{2+} and Fe^{3+} ions by adding the ferric chloride hexahydrate and ferrous chloride tetrahydrate. Moreover, the various Mn ion (Manganese (II) chloride tetrahydrate) contents were added into magnetic PCH to enhance the magnetic properties and testing methods to evaluate the moisture adsorption performance. Subsequently, these as-synthesized mesoporous materials were blended with polylactide, and the properties concerning the capability of polylactide-magnetic PCHs nanocomposites in anti-corrosion packaging were investigated.

4.3 Experimental

Materials

Montmorillonite (MMT) was provided by Pai Kong Nano Technology Co., Ltd. The cation exchange capacity (CEC) of MMT is 102 mmol/100g of clay.

Cetyltrimethylammonium [$\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3$] bromide (CTAB) was supplied by Fluka. Dodecylamine, $\text{C}_{12}\text{H}_{27}\text{N}$, (MW=185.35), (98% purified) was supplied by Aldrich. Tetraethyl orthosilicate (TEOS), (MW=208.33), Ammonium hydroxide (NH_4OH), Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and Manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) were purchased from Fluka. Methanol (CH_3OH) was supplied by Lab Scan and Hydrochloric acid (HCl) was supplied by Carlo Erba. Polylactide 4042D (PLA) was supplied by NatureWorks Co., Ltd and Polyethylene glycol (PEG) was supplied by Sigma.

Purification and pH Adjustment of Na-Monmorillonite

Na-Monmorillonite was pulverized and sieve through 325 mesh. Three 10-g of the passing part were purified by centrifugation and then washed with distilled water until the pH value is near 7. After that, centrifugation was applied. Again, the same amount of distilled was added, and then the pH of each sample was adjusted to 9.0 by using dilute HCl and NaOH solutions. This procedure was repeated for 48 h to equilibrate the pH of each sample. The samples were air-dried overnight and again pulverized in a mortar.

Synthesis of Porous Clay Heterostructures (PCHs)

Na-Monmorillonite was converted into a Quaternary ammonium exchange form by ion exchange with 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 following which TEOS was added (at molar ratio of organoclay:dodecylamine:TEOS was 1:20:200). 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 PCH. The surfactant was removed from the as-synthesized PCH by solvent extraction using methanol/HCL solution. Typically, 1 g of the as-synthesized PCH 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 air-dried at room temperature overnight.

Preparation of Magnetic PCHs

Ferric chloride hexahydrate and ferrous chloride tetrahydrate are used as iron sources which they were added in PCH at 20 wt%. Manganese (II) chloride tetrahydrate is used as manganese sources which it was added in PCH at 5, 10, 15 and 20 wt%. Aqueous ammonia is used as the precipitator. Distilled water is used as the solvent. Before the reaction, N₂ gas was flown through the reaction medium. The reaction was operated in a closed system to provide a nonoxidation environment. NH₄OH was slowly injected into PCH which added ferric chloride hexahydrate,

ferrous chloride tetrahydrate and manganese (II) chloride tetrahydrate under stirring 30 min. The dispersion was centrifuged at 3000 rpm for 20 min. After precipitation, the Fe_2O_3 particles in PCH were repeatedly washed and filtered before drying at room temperature in air atmosphere to form powders.

Physical Measurements

Powder X-ray diffraction patterns were measured on a Bruker AXS Model D8 Discover diffractometer with Ni-filtered Cu K_α radiation operated at 40 kV and 40 mA. The powder samples were observed on the 2θ range of 1.0-10 degree with a scan speed 0.5 degree/step and a scan step of 0.02 degree/step.

N_2 adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Powder samples were degassed at 150°C during 15 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 JEOL JSM-5410 lv Model. The specimens were coated with platinum under vacuum before observation 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.

UV/VIS Spectrophotometer was recorded on a UV/vis spectrophotometer 2550 (Shimadzu) scanning in the range of 200-1000 nm at room temperature. Experiments were performed in a solid stub.

X-Ray Fluorescence Spectrometer was carried out using a Phillips PW2400 and Oxford ED-2000 instrument.

Vibration Sample Magnetometer was performed on LakeShore-7404 model with continuous mode, Maximum field 10 kOe, and Ramp rate: 50.63 Oe/s.

Moisture adsorption was carried out by weight dried PCH and Magnetic PCHs before and after test. The products are exposed to a humid atmosphere and will take up moisture until a state of equilibrium is reached.

Chemical Analysis

FT-IR spectra of organoclay, PCHs, and magnetic PCHs 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 was investigated by using FTIR technique.

4.4 Results and Discussion

A. The Interlayer Distance of Montmorillonite, Organoclay and PCH

A corresponding XRD pattern of the samples are shown in Table 4.1 and Figure 4.1, the basal spacing of MMT was 1.20 nm and show the presence of the (001) reflection peak. After MMT was treated with cetyltrimethylammonium bromide (CTAB) to obtain organoclay, the peak of starting clay at $2\theta = 7.34^\circ$ ($d = 1.20$ nm) disappeared, two strong peaks are observed at lower angle which are $2\theta = 4.66^\circ$ ($d = 1.89$ nm) and $2\theta = 2.36^\circ$ ($d = 3.74$ nm) as a consequence of the successful intercalation of cationic surfactant in the interlayer of MMT, resulting in the increasing of distance between clay layers. The results are shown in Table 4.1

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) was introduced to polymerize surrounding the surfactant micelles in the galleries of clay. By solvent extraction method, the surfactant templates were removed from as-synthesized PCH, resulting in the formation of porous structures. After the as-synthesized PCH was extract with solvent, A strong peak observed at the angle of $2\theta = 2.54^\circ$ ($d = 3.47$ nm) showed the formation of porous structures.

Table 4.1 The basal spacing of montmorillonite and organic

| Sample | 2 θ (degree) | d-value (nm) |
|-----------------|---------------------|--------------|
| Montmorillonite | 7.34 | 1.2 |
| Organoclay | 2.36 | 3.74 |
| PCH | 2.54 | 3.47 |

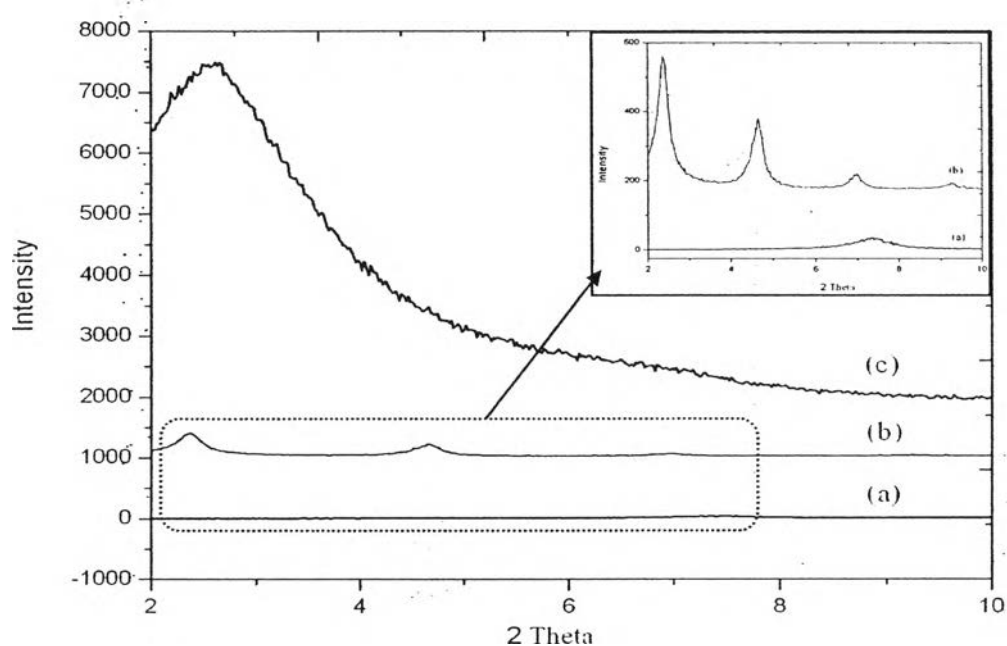


Figure 4.1 The XRD patterns of (a) montmorillonite, (b) Organoclay and (c) PCH. The insertion show the XRD patterns of (b) Organoclay, and (c) PCH (zoom in).

B. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The FTIR spectrum of MMT is given in Figure 4.2 (a). The broad peak around 3446 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 SiO_4 units, the asymmetric and symmetric stretching vibrations of the Si-O-Si linkage, respectively. The peak at 1635 cm^{-1} may be due to the presence of adsorbed water. The presence of surfactant was evidenced by FTIR spectra of organoclay (Figure 4.2(b)) indicating the asymmetric and symmetric vibrations of methyl and methylene groups of cetylrimethyl ammonium ion at 2918

and 2850 cm^{-1} , respectively. The FTIR spectrum of PCH (Figure 4.2(c)) is different from starting MMT indicated by the absence of peak at 1000 cm^{-1} . So it roughly infers that the structure of starting clay was changed after the modification.

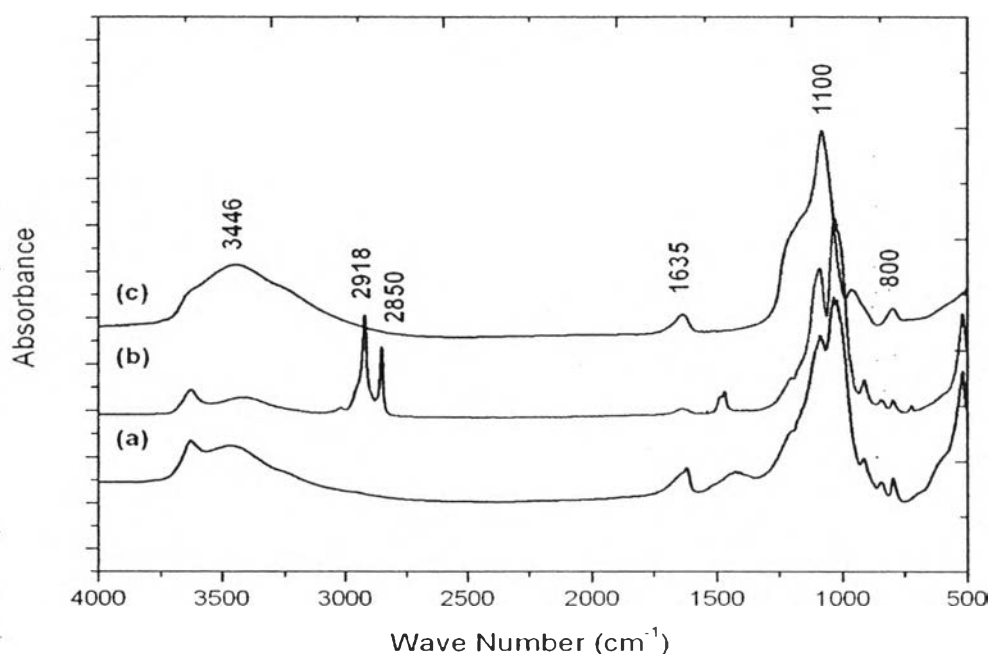


Figure 4.2 FTIR spectra of (a) MMT, (b) Organoclay, and (c) PCH.

C. Pore Characterization of PCH and Magnetic PCHs

Table 4.2 shows the results of N_2 adsorption. The BET surface area of MMT was $21.06\text{ m}^2/\text{g}$ while the surface areas of PCH increased significantly from pristine clay. The results showed that PCH had surface areas of $659.30\text{ m}^2/\text{g}$, average pore diameter was 3.07 nm , and pore volume was 0.51 cc/g , magnetic PCHs had surface areas of $241\text{-}351.05\text{ m}^2/\text{g}$, average pore diameter in the range of $5.33\text{-}7.15\text{ nm}$ and pore volume of $0.40\text{-}0.46\text{ cc/g}$, respectively. Magnetic PCHs exhibited a high average pore diameter and a less surface area as compared with the PCH (Table 4.2) because the pore structures were collapsed and the Fe and Mn ion can aggregate by the hydrolysis of iron and manganese salts.

The isotherm of MMT belongs to type II characteristic of nitrogen adsorption on macroporous adsorbents. The isotherms of PCH and magnetic PCHs are shown in Figure 4.3 which were abruptly increased in nitrogen adsorption at low

partial pressure and gradually increased to medium partial pressure (P/P_0 :0.05-0.3) suggested that these materials possess supermicropore to small mesopore region, belong to type IV, corresponding to mesoporous adsorbents.

Table 4.2 Porosity characteristics of montmorillonite PCH and magnetic PCHs

| Sample | Multipoint BET surface area (m^2/g) | Average pore diameter (nm) | BJH pore volume (cc/g) |
|----------------|---|----------------------------|--|
| Monmorillonite | 21.06 | 23.96 | 0.15 |
| PCH | 659.30 | 3.07 | 0.51 |
| Fe:Mn (20:0) | 351.05 | 5.33 | 0.46 |
| Fe:Mn (20:5) | 306.00 | 5.89 | 0.44 |
| Fe:Mn (20:10) | 241.15 | 6.69 | 0.40 |
| Fe:Mn (20:15) | 241.11 | 6.84 | 0.41 |
| Fe:Mn (20:20) | 241.00 | 7.15 | 0.42 |

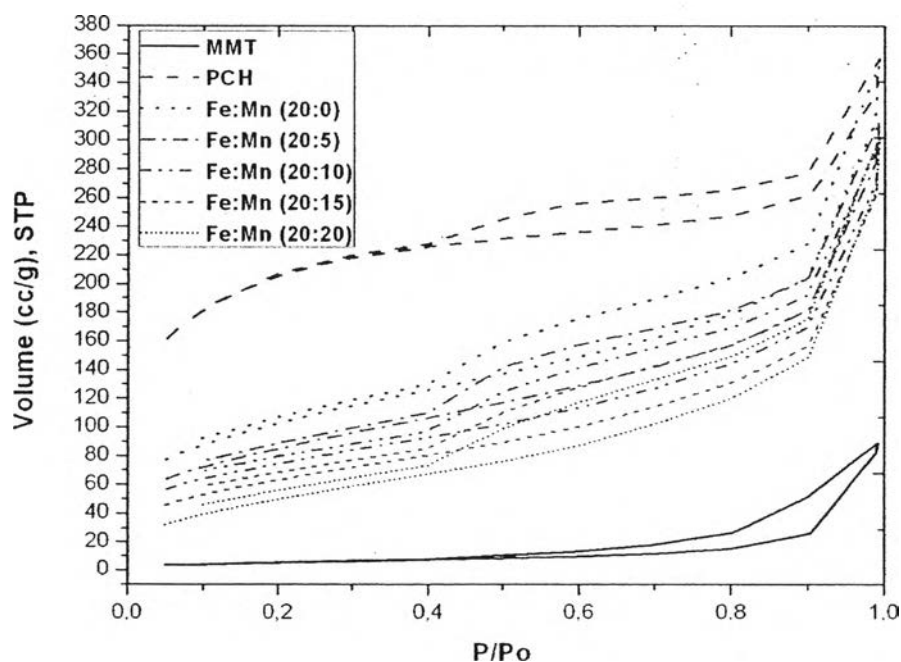


Figure 4.3 N_2 adsorption-desorption isotherms of montmorillonite, PCH, and magnetic PCHs.

D. The UV/vis Absorbance Spectra Analysis

In addition, to ensure the existence of ferric, ferrous and manganese ion in the octahedral sheet, UV/vis spectrophotometer was carried out as well. The basic structural SiO_4 units of tetrahedral sheets in the clay lattice do not absorb light in the wavelength ranging from 200 to 800 nm, except when the transition metal ions in the silicate structure is exchanged. Transition metal cations (e.g. Fe^{3+} and Al^{3+}) appearing at both the crystal edges and the planar surfaces of smectite clay can act as an oxidizing agent (electron acceptor). Figure 4.4 shows the absorbance spectra of MMT, PCH, and magnetic PCH (Fe:Mn). The appearance of spectrum at 242 nm and broad spectrum in the range 200-300 nm points to the charge transportation from O^{2-} , OH^- , or H_2O to the iron and manganese ion, respectively in the octahedral layer of the clay mineral.

The magnetic PCHs which have both Fe and various amount of Mn present a similar spectrum to the magnetic PCH which has only Fe, which indicated that no interaction occurs between them under the simple procedure of doping [10].

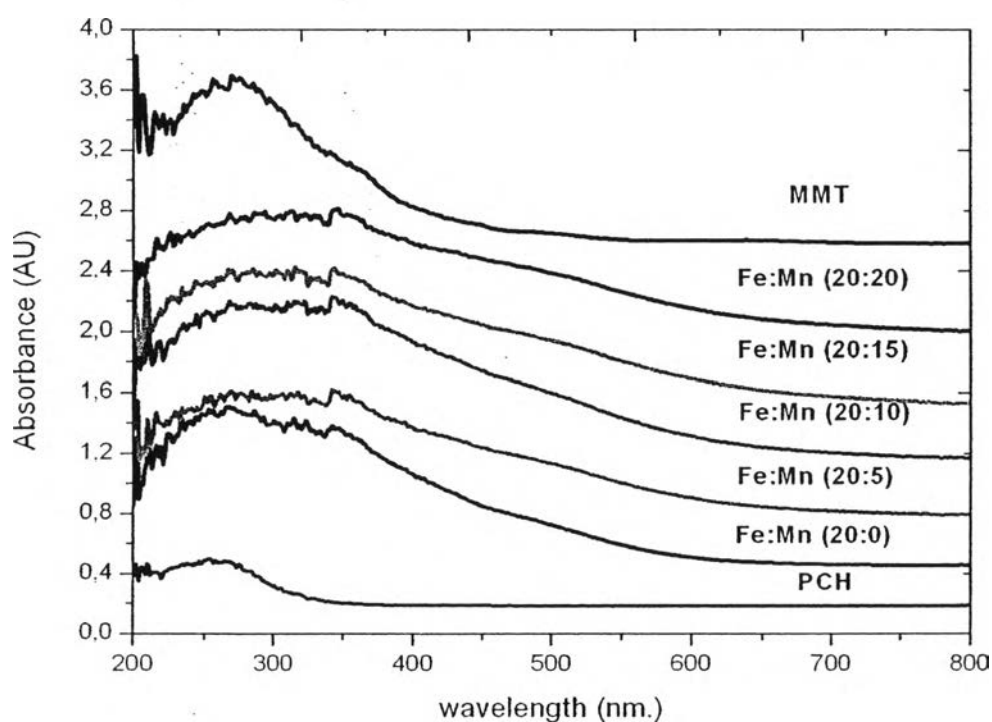


Figure 4.4 UV/vis absorbance spectra of as-synthesized PCH, magnetic PCHs (Fe:Mn), and MMT.

E. The X-ray Fluorescence Analysis

Table 4.3 shows the results of chemical composition of PCH and Magnetic PCHs. Magnetic PCHs had a higher iron oxide and a less silicon tetra oxide as compared with the PCH due to the substitution of Fe and Mn in PCH. The increasing of Mn ratio yield the higher manganese oxide and less iron oxide resulted from the substitution of Mn in PCH-Fe.

Table 4.3 Chemical Composition of PCH and Magnetic PCHs

| Sample | Chemical Composition (% wt) | | | | | | | |
|------------------|-----------------------------|--------------------------------|------------------|-----------------|------------------|--------|------------------|--------------------------------|
| | MgO | Al ₂ O ₃ | SiO ₂ | SO ₃ | K ₂ O | CaO | MnO ₂ | Fe ₂ O ₃ |
| PCH | 0.19 | 0.99 | 74.44 | < 0.01 | 0.03 | 0.02 | < 0.01 | 0.63 |
| Fe:Mn (20:0) | 0.22 | 1.02 | 68.83 | < 0.01 | 0.02 | 0.02 | 0.03 | 13.93 |
| Fe:Mn (20:5) | 0.20 | 0.99 | 67.29 | < 0.01 | 0.03 | 0.03 | 3.51 | 13.01 |
| Fe:Mn (20:10) | 0.18 | 0.93 | 61.56 | 2.10 | 0.02 | 0.02 | 6.67 | 12.40 |
| Fe:Mn (20:15) | 0.21 | 0.95 | 61.94 | < 0.01 | 0.01 | 0.01 | 8.96 | 11.39 |
| Fe:Mn (20:20) | 0.18 | 0.94 | 60.11 | 0.03 | 0.02 | < 0.01 | 11.90 | 10.57 |

F. Moisture Adsorption Analysis

Figure 4.5 and Table 4.4 shows the results of moisture adsorption of Magnetic PCHs and as-synthesized PCH. Magnetic PCHs adsorbed higher moisture as compared with the PCH due to the Fe and Mn ions can improve the hydrophilicity. Moisture adsorption of magnetic PCHs decreased when Mn ion increased because iron oxide which reacted with water to form hydrated iron oxide in magnetic PCHs decreased corresponding to XRF result.

From the moisture adsorption results (Table 4.4), The Magnetic PCHs at the molar ratio of iron and manganese is 20/0 (Fe:Mn = 20:0) is suitable to modify their

surfaces by VCI because of the highest moisture adsorption or can be implied that the doping by Mn is not practical to PCH surface for attached VCI functional group.

Table 4.4 Moisture adsorption (%) of PCH and Magnetic PCHs

| Sample | Moisture adsorption (%) |
|---------------|-------------------------|
| PCH | 0.46 |
| Fe:Mn (20:0) | 5.55 |
| Fe:Mn (20:5) | 3.41 |
| Fe:Mn (20:10) | 2.98 |
| Fe:Mn (20:15) | 3.35 |
| Fe:Mn (20:20) | 3.14 |

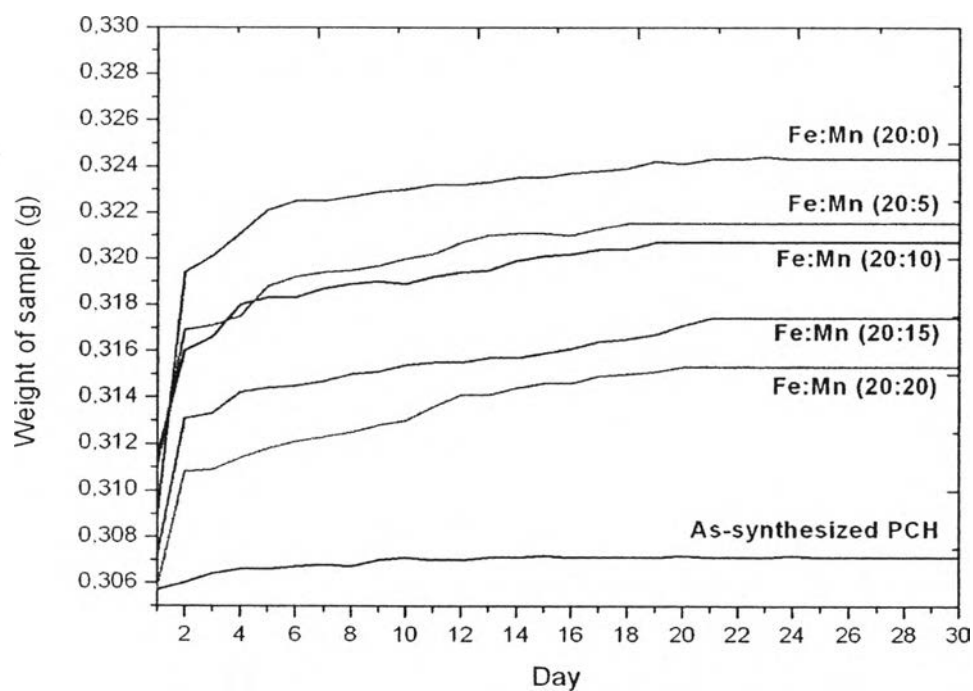


Figure 4.5 Moisture adsorption of PCH, and Magnetic PCHs.

G. Vibration Sample Magnetometer

The magnetization curves for Magnetic PCHs with various Mn ion concentrations are given in Figure 4.6. Magnetic PCHs were the paramagnetic materials. The magnetic moment induced by the applied field is linear in the field strength and rather weak. Paramagnets do not retain any magnetization in the absence of an externally applied magnetic field, because thermal motion causes the spins to become randomly oriented without it. Thus the total magnetization will drop to zero when the applied field is removed. Even in the presence of the field there is only a small induced magnetization because only a small fraction of the spins will be oriented by the field. This fraction is proportional to the field strength and this explains the linear dependency

The saturation magnetization (M_s) value of magnetic PCH are shown in Table 4.5 It was found that M_s value of magnetic PCH increased with the higher Mn concentrations, range from 0.07 emu/g for 0 wt%, 0.10 emu/g for 5 wt%, 0.11 emu/g for 10 wt%, 0.14 emu/g for 15 wt% and 0.16 emu/g for 20 wt% of Mn. The increased in M_s with Mn ion content could be explained in terms of resultant of sublattice magnetic moments. The spontaneous magnetization in spinel iron oxide is a result of the interactions of transition metal cations and oxygen anions. Consequently, the magnetic properties can be considered to be the sum of the magnetic interactions on the tetrahedral A -site sublattice and the octahedral B -site sublattice and these two sublattices are oppositely aligned and their resulting magnetic moment determines the net magnetic moment of iron oxide. Any substitution of metal ions in iron oxide prefers to occupy tetrahedral sites and reduces magnetic moment on the A -site sublattice and hence the resulting net magnetic moment will be increased [11].

Table 4.5 Magnetization and Coercivity of Magnetic PCH with various Mn ion contents

| Sample | Magnetization (emu/g) | Coercivity (G) |
|---------------|-----------------------|----------------|
| Fe:Mn (20:0) | 0.07 | 62.80 |
| Fe:Mn (20:5) | 0.10 | 101.84 |
| Fe:Mn (20:10) | 0.11 | 64.55 |
| Fe:Mn (20:15) | 0.14 | 28.38 |
| Fe:Mn (20:20) | 0.16 | 77.51 |

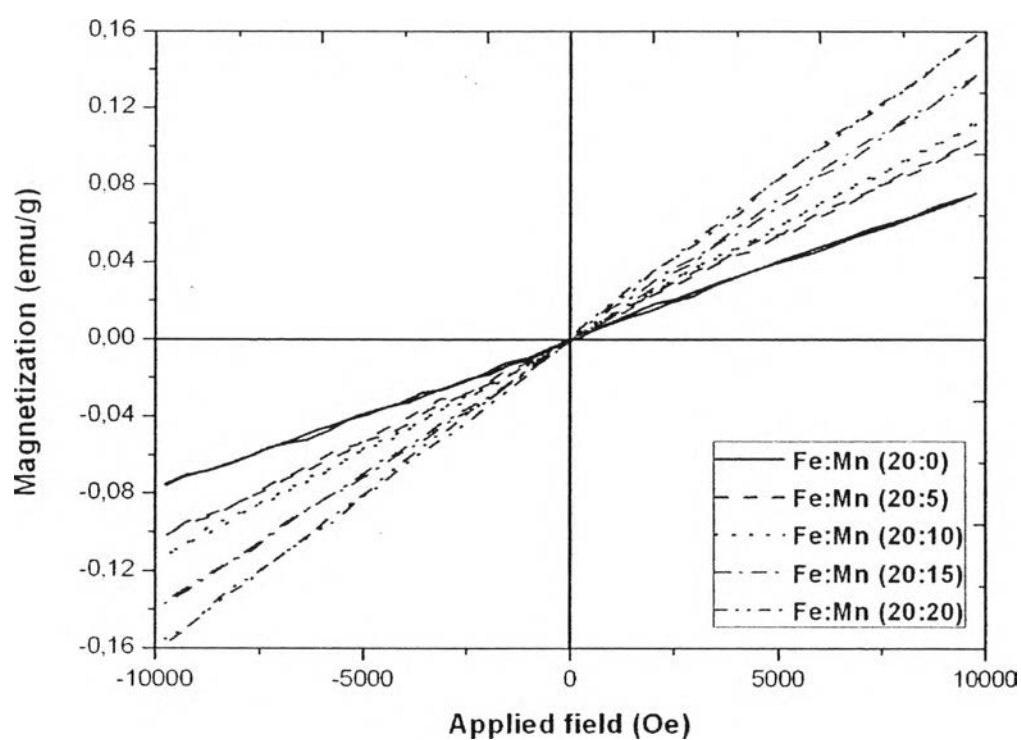
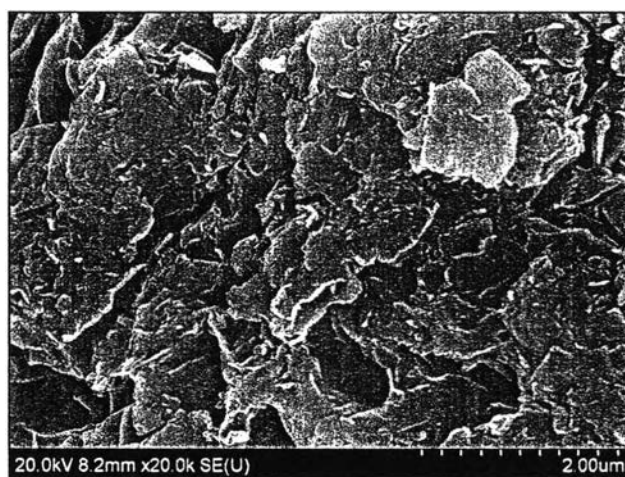


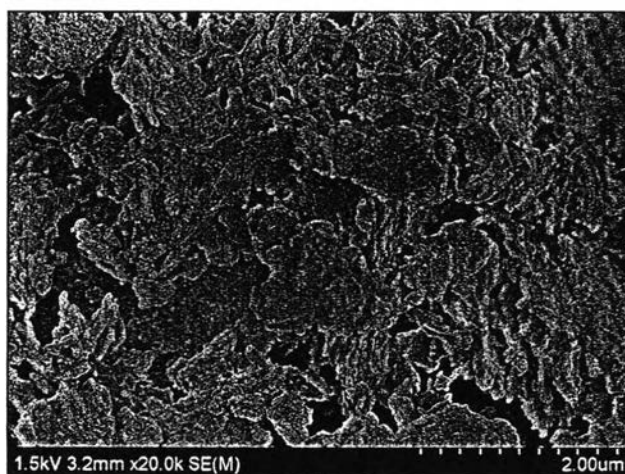
Figure 4.6 Magnetization curves of Magnetic PCH with various Mn ion contents.

H. The Morphology Analysis

Surface morphology's the MMT exhibits a layered or plate-like structure in SEM image as shown in Figure 4.7(a). After modification, the SEM image of PCH in Figure 4.7(b) reveals a similar morphology to starting clay but more surface roughness than MMT. According to N_2 adsorption-desorption results in Table 4.2 and Figure 4.3, the surface areas of PCHs increased significantly compared to those of pristine clay.



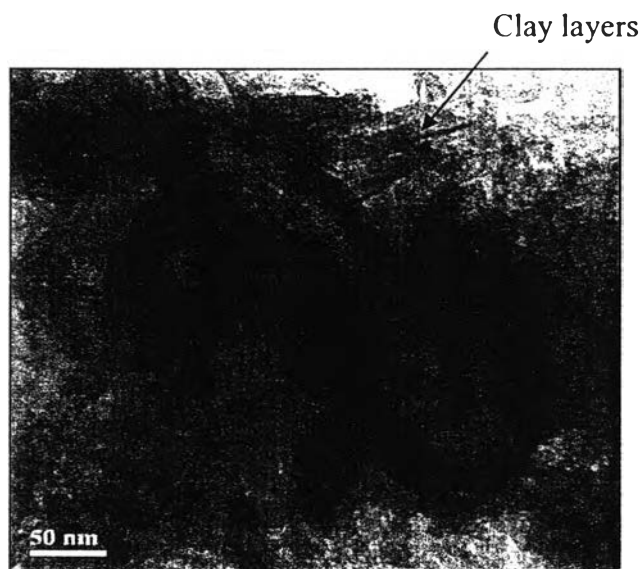
(a)



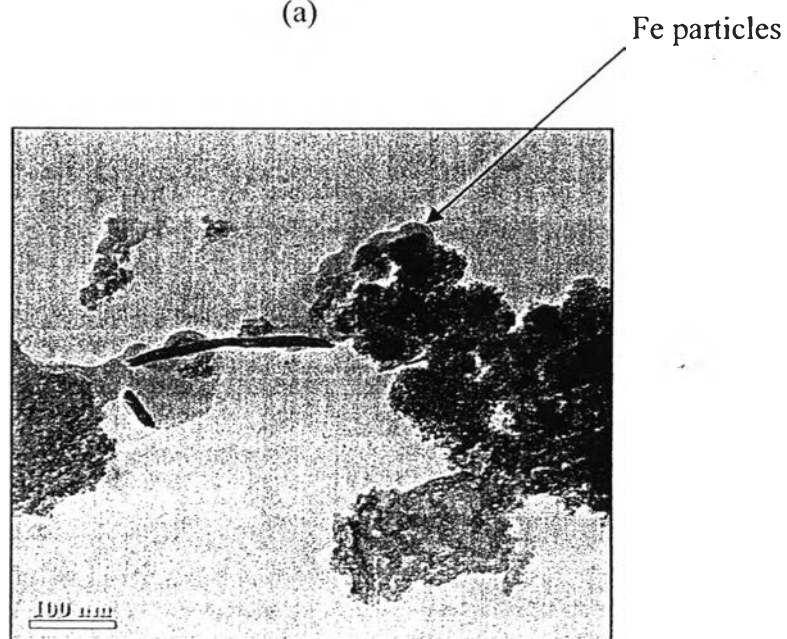
(b)

Figure 4.7 SEM images of (a) Montmorillonite, and (b) PCH.

In the TEM image provided in Figure 4.8, the clay layers were discernible as solid dark lines which were easily observed. The framework pore orientation was not persistent. However, the presence of the dispersion on the clay layers in Figure 4.8 (b) and (c), the Fe and Mn particles were discernible as dark spots and it can be seen that the iron co-aggregates.



(a)



(b)

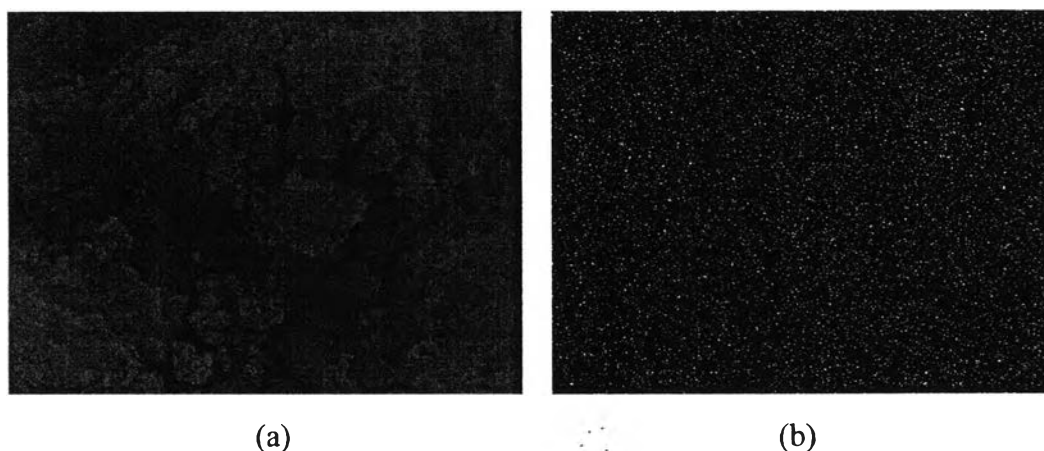


Figure 4.10 SEM image and consistent EDX micrograph of 20%wt Mn ion in PCH (a) SEM image, and (b) Mn mapping.

4.5 Conclusions

Porous clay heterostructures (PCHs) derived from Na-montmorillonite clay were synthesized by a surfactant directed assembly of silica species within the clay galleries. PCH was modified the surface by ferric chloride hexahydrate and ferrous chloride tetrahydrate to obtain the magnetic PCH. The various Mn ion contents were added into magnetic PCH to enhance the magnetic properties. From the analysis of N_2 adsorption-desorption data, the results showed that PCH had surface areas of 659.30 m²/g, average pore diameter was 3.07 nm, and pore volume was 0.51 cc/g, magnetic PCHs had surface areas of 241-351.05 m²/g, average pore diameter in the range of 5.33-7.15 nm and pore volume of 0.40-0.46 cc/g, respectively. The isotherms of PCHs and magnetic PCHs belong to type IV, corresponding to mesoporous adsorbents. When montmorillonite was treated with CTAB, the distance between clay layers increased. A strong peak is observed after the as-synthesized PCH was extract with solvent, it suggests that the existence of porous formation as investigated by XRD. SEM images, EDX micrographs and UV adsorption of magnetic PCHs showed incorporation of Fe ion and Mn ion in PCH is successful. From the moisture adsorption analysis, the Magnetic PCHs at the molar ratio of Fe:Mn = 20:0 is suitable to modify their surfaces by VCI because of the highest moisture adsorption or can be implied that the doping by Mn is not practical to PCH

surface for attached VCI functional group. Magnetic PCHs were the paramagnetic materials and the saturation magnetization (M_s) value of magnetic PCH increased with higher Mn concentrations as investigated by VSM.

4.6 Acknowledgements

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4.7 References

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