



CHAPTER IV

SYNTHESIS OF CHROMOPHORES MODIFIED POROUS CLAY HETEROSTRUCTURE

4.1 Abstract

Because of the advantage of porous clay heterostucture (PCH) and functionalized PCH on barrier properties, high surface area and ability of gas absorption, porous material is the one of most popular starting materials for many application. In this work, the functionalized PCH with amino group (APPCH) and PCH were modified with pH dye either methyl red or bromothymol blue for using as colorimetric indicator. To confirm the formation of porous structure, the products were characterized by N₂ adsorption-desorption, XRD, SEM and FTIR techniques. The results revealed that PCH had the high surface areas of 524.1 m²/g, average pore diameter of 4.85 nm and pore volume of 0.64 cc/g while the functionalized PCH (APPCH) had the decrease of surface area and pore volume in the range of 119.8-320.5 m²/g and 0.33-0.42 cc/g, respectively. The rugged surface of SEM image and no observed the obvious peak from XRD spectra was used to confirm the porous structure in APPCH and PCH. The incorporation of methyl red in APPCH and bromoyhymol blue in PCH was investigated by N₂ adsorption-desorption, XRD and SEM. The results showed that surface area and pore volume of APPCH and PCH decreased after modified with pH-dye indicated that the incorporation of pH dye in APPCH and PCH was successful.

Keywords: Porous clay heterostucture (PCH)/ chromophores

4.2 Introduction

Porous Clay Heterostructure (PCH) is a porous material that has been developed due to the special properties i.e. improves the ability of adsorption by high surface area. PCH can be prepared by using surfactant incorporated within the

galleries of clay. Cationic surfactants will intercalate between the sheets of clay. Then PCH is synthesized by polymerization of the silica source such as tetraethoxysilane (TEOS) in the presence of surfactant micelles. However, in the preparation of PCHs, calcination at high temperature (600-650°C) or solvent extraction method are necessary to remove the surfactant in order to obtain complete porous silica structure.

Subsequently, to produce PCH with organic-inorganic hybrid structure, the structure of inorganic frame works is combined with organic group in PCH in order to provide the high adsorption property for gas molecules and high selectivity for organic compound.

Due to the advantage of PCH and functionalized PCH, the porous materials were widely used in order to enhance the properties for the desired application. Recently, porous material is the one of most popular starting materials for preparing nanocomposite films by incorporating with community plastic in order to develop active and smart packaging. Because of the improvement in the properties of the nanocomposite films will be obtained from the superior properties of porous materials such as barrier properties improvement, high surface area and ability of gas absorption.

The aim of this studied was to enhance the colorimetric properties of chromophores and barrier properties of PCH and functionalized PCH (APPCH) by modification of chromophores modified PCH and functionalized PCH for using in film packaging. Subsequently, the obtained APPCH-MR was blended with polypropylene (PP) and PCH-BTB was blended with low density polyethylene (LDPE) in order to produce the nanocomposite films for smart packaging application.

4.3 Experimental

A. Preparation of Organomodified Bentonite

A 0.1 M solution of the surfactant (Cetyl trimethyl ammonium bromide, CTAB) was prepared. 3 g of clay (Sodium bentonite, Na-BTN) was added to 50 ml of this solution and the mixture was stirred for 24 h at 50°C. After the exchange

cation reaction, the clay was filtrated from the solution and washed with the mixture of distilled water and methanol (1:1) until pH of 9 was reached. The modified clay was dried at 50°C for 24 h and ground into powder using centrifugal ball mill with 400 rpm for 30 min before screened through a mesh #325.

B. Preparation of Functionalized Porous Clay Heterostructure

The synthesized organoclay was added to a neutral amine such as dodecylamine and the mixture of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) in the follow molar ratio: organoclay/dodecylamine/TEOS: APTES = 1/20/150. In first step, organoclay was mixed with dodecylamine and stirred at 50°C for 30 min. After that the mixture of TEOS and APTES in mole fraction of 0.97: 0.03, 0.95: 0.05 and 0.90: 0.10 was added to the mixture allowed reacting for 4 h at room temperature under continuous stirring by co-condensation method. After reaction, the modified clay was filtrated from the solution and washed with methanol. The modified clay was dried at room temperature for 24 h. For extraction process, 1 g of as-synthesized PCH was added to 45 ml of methanol and 5 ml of concentrated HCl and refluxed for 2 h. Then, the modified clay was filtered off and washed with methanol and water and air-dried at room temperature overnight before screened through a mesh #325. The modified clay by APTES was named APPCH.

C. Preparation of Porous Clay Heterostructure (PCH)

The obtained organoclay prepared with the surfactant (Cetyl trimethyl ammonium chloride, CTAC) was added to a neutral amine such as dodecylamine and tetraethoxysilane (TEOS) in the follow molar ratio: organoclay/dodecylamine/TEOS = 1/20/150. In first step, organoclay was mixed with dodecylamine and stirred at 50°C for 30 min. After that tetraethoxysilane (TEOS) was added to the mixture allowed reacting for 4 h at room temperature under continuous stirring. After reaction, the modified clay was filtrated from the solution and washed with methanol. The modified clay was dried at room temperature for 24 h. For extraction process, 1 g of as-synthesized PCH was added to 45 ml of methanol and 5 ml of concentrated HCl and refluxed for 2 h. Then, the modified clay was filtered off and washed with methanol and water. After that, it was air-dried at room temperature overnight before screened through a mesh #325.

D. Preparation of Chromophores Modified Functionalized PCH

The functionalized PCH from 3.3.1.2 (APPCH) was consequently modified with pH dye (methyl red) at various weight ratio of APPCH: dye (10:1, 20:1 and 30:1). First, methyl red is dissolved in 0.05M HCl solution. Then, methyl red solution was added into the functionalized PCH under continuous stirring to obtain chromophores modified functionalized PCH. After that the modified clay was filtered off and dried in vacuum oven before screened through a mesh #325. The methyl red modified APPCH was named APPCH-MR.

E. Preparation of Chromophores Modified PCH

The PCH was modified with pH dye (bromothymol blue) at weight ratio of PCH: dye of 10:1, 20:1 and 30:1. First, bromothymol blue was dissolved in solution of 0.05 M NaOH. Then, bromothymol blue solution was added into the PCH under continuous stirring to obtain chromophores modified PCH. After that the modified clay was filtered off and dried in vacuum oven before screened through a mesh #325. The bromothymol blue modified PCH was named PCH-BTB.

F. Characterizations

The X-ray diffractometer using Bruker AXS model Diffractometer D8 was used to identify the interlayer spacing of Na-bentonite and modified clay. The experiment was performed in the 2θ range of 2-10 degrees with scan speed 2 degree/min and scan step 0.01 degree.

The functional group of Na-bentonite and modified clay were identified by Nicolet Nexus 670 FTIR spectrometer. FTIR was carried out in the transmission mode with 64 scans between 4000-400 cm^{-1} at a resolution of 4 cm^{-1} .

The surface morphology of Na-bentonite and modified clay were observed by using S-4800 field emission scanning electron microscope.

The pore size, surface area and pore volume of porous samples were measured and the influence of incorporating functional group and pH dye into porous sample was determined by nitrogen adsorption-desorption isotherms on surface area analyzer using Quantachrome Autosorb-1. The samples were degassed at 250°C for 17 h in a vacuum furnace before analysis.

The pH dye (methyl red) adsorbed onto the APPCH compared to PCH was measured. 0.1 g of APPCH was mixed with 50 ml aqueous solution containing 2 x

10^{-4} M MR. After one day, the residual MR concentration was determined compared with the initial concentration of MR by UV-Vis using Shimadzu Model UV-1800 at 524 nm. The amount of methyl red (MR) adsorbed onto the APPCH compared to PCH was calculated following equation [6].

$$q = \frac{V (C_0 - C)}{mS}$$

Where, q	=	The amount of MR adsorbed onto porous sample (mol/m ²)
C ₀	=	The initial concentration of MR solution (mol/l)
C	=	The residual concentration of MR solution (mol/l)
V	=	The solution volume (l)
m	=	Mass of porous sample (g)
S	=	BET surface area of porous sample (m ² /g)

4.4 Result and discussion

A. Characterization of the organomodified bentonite (OBTN), Porous Clay Heterostructure (PCH) and Functionalized Porous Clay Heterostructure (APPCH)

The sodium bentonite clay (Na-BTN) and the obtained modified clay (OBTN, PCH and APPCH) were shown in Figure 4.1.

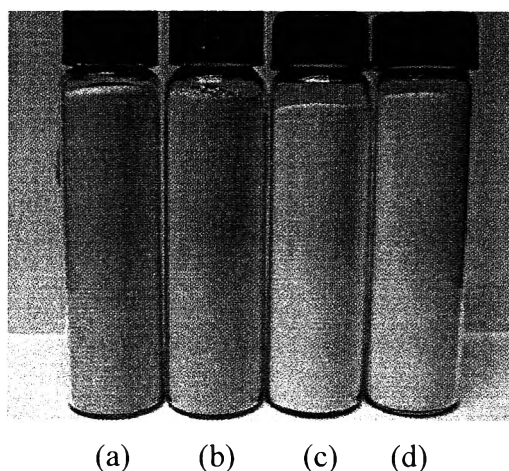


Figure 4.1 (a) Na-BTN, (b) OBTN, (c) PCH and (d) APPCH.

The organomodified bentonite (OBTN) was confirmed the expansion of sodium bentonite (Na-BTN) layers by incorporating of cationic surfactant and studied the effect of using different surfactant by XRD. Figure 4.2 showed XRD results of Na-BTN and OBTN. The XRD pattern showed the presence of the (001) reflection peak. The d_{001} peak of Na-BTN at $2\theta = 7.10^\circ$ which corresponded to the basal spacing of 1.24 nm (Figure 4.2 a). After modified Na-BTN with cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), OBTN showed the d_{001} peak at lower angle of 2.24° which corresponded to the basal spacing of 3.93 nm (Figure 4.2 b) indicating the increasing the basal spacing of clay layers due to ammonium ions from cationic surfactant intercalated into the silicate layers. In addition, the XRD result showed that the obtained OBTN synthesized from the surfactant, cetyl trimethyl ammonium chloride (CTAC) as shown in Figure 4.2 c showed the increasing the basal spacing of clay layers but the d-spacing less than the OBTN synthesized from CTAB [1].

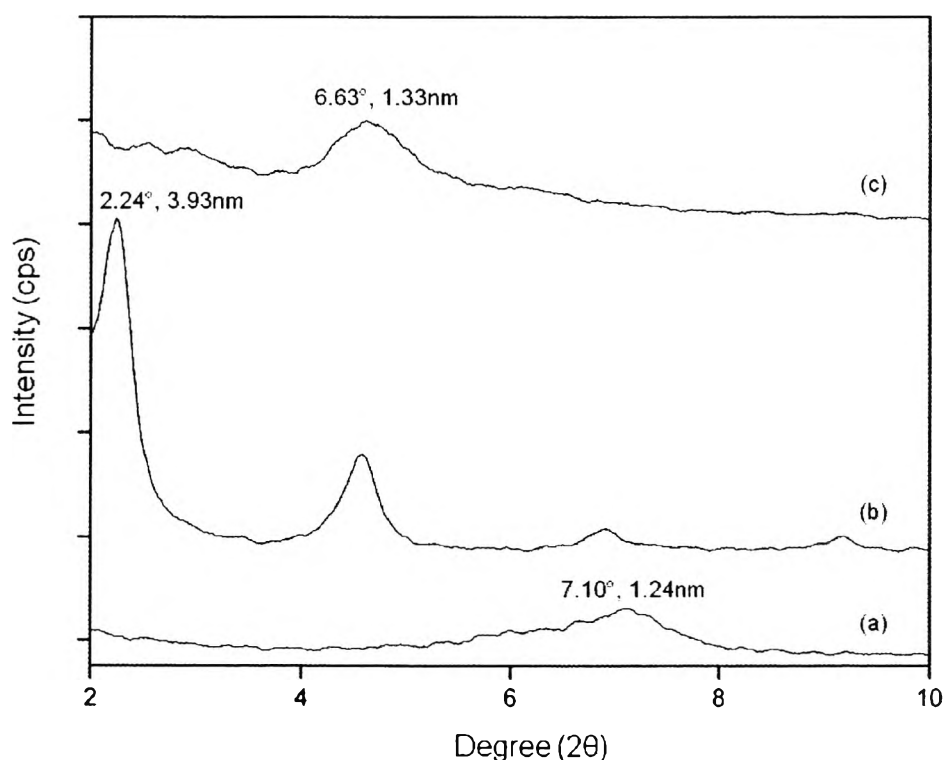


Figure 4.2 The XRD patterns of (a) Na-BTN, (b) OBTN (CTAB) and (c) OBTN (CTAC).

From the FTIR results (Figure 4.3), the FTIR spectrum of Na-BTN (Figure 4.3 a) showed the peak at around 3500 cm^{-1} assigned to the stretching vibration of the silanol associated with the silica structure and the peak at around 1000 cm^{-1} assigned to the stretching vibration of the SiO_4 units. The peaks at around 1100 and 800 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the Si-O-Si linkage. The presence of surfactant in the layer of BTN was indicated by FTIR spectra of OBTN (Figure 4.3 b). The peaks at 2919 and 2850 cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of methyl and methylene groups of hexadecyltrimethylammonium ion respectively. The FTIR spectra of PCH (Figure 4.3 c) and APPCH (Figure 4.3 d) were different from Na-BTN at the absence of the peak at 1000 cm^{-1} because of the changing of clay structure after modification. In addition, the peak at around 1510 cm^{-1} were confirmed the organic group ($-\text{NH}_2$) from APTES molecule in the structure of APPCH [2].

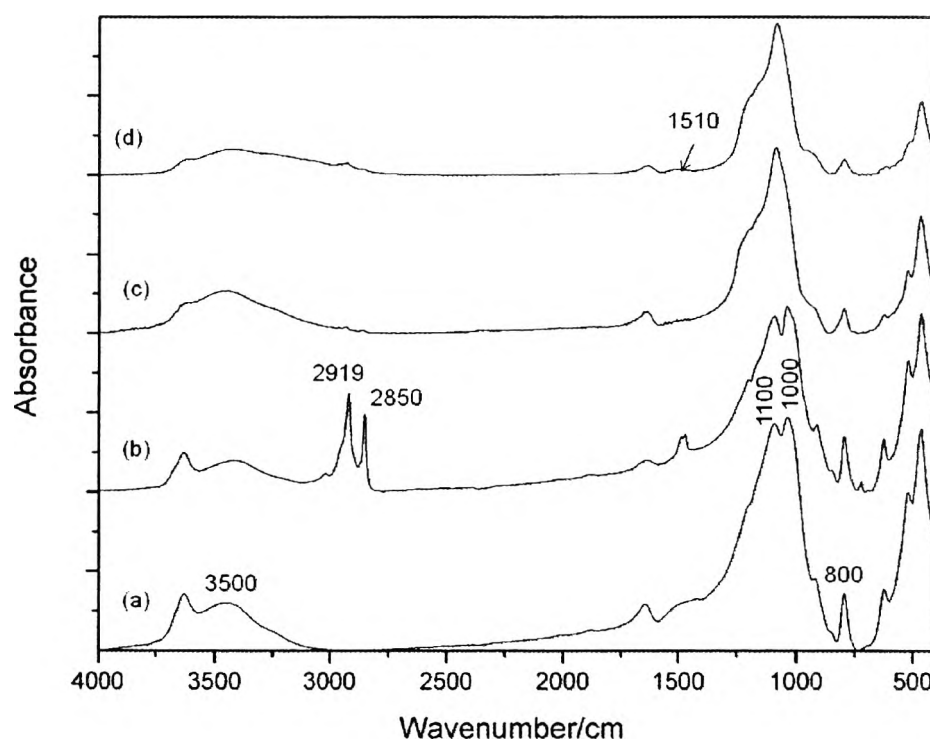
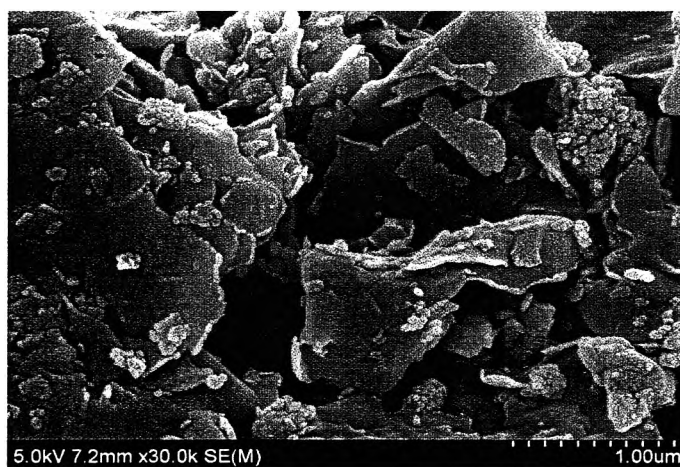
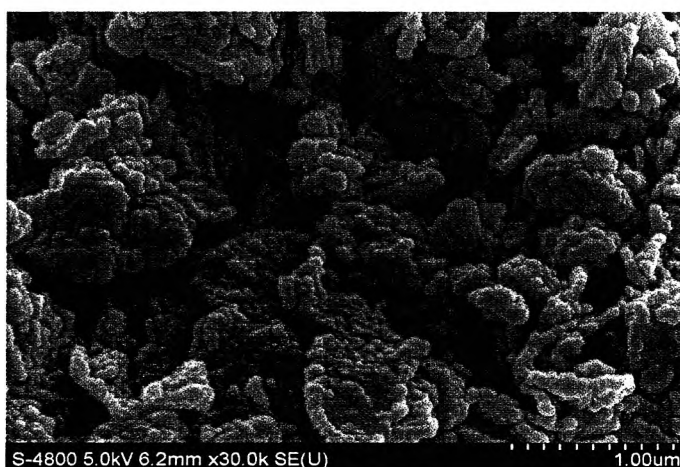


Figure 4.3 Fourier transform infrared spectroscopy spectra of (a) Na-BTN, (b) OBTN, (c) PCH and (d) APPCH.

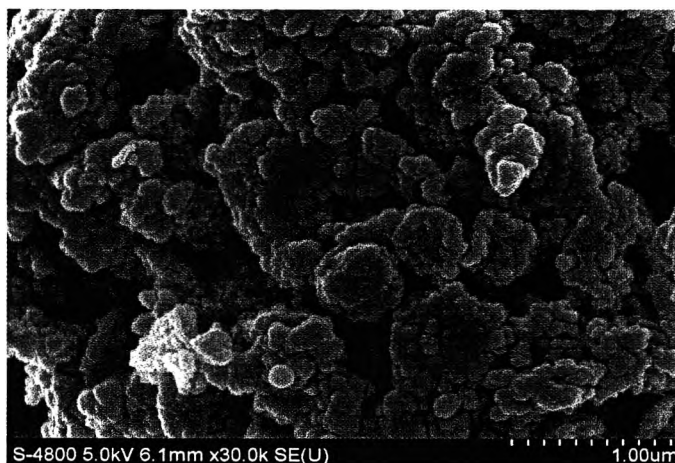
The morphology of Na-BTN and modified clay were characterized by SEM image. The flat plate structure of Na-BTN was observed (Figure 4.4 a). After porous samples were synthesized within the galleries of bentonite by the polymerization of tetraethoxysilane (TEOS) in the presence of surfactant micelles, the rugged surface of PCH (Figure 4.4 b) and APPCH (Figure 4.4 c) were presented because of the formation of pore structure in the galleries of clay [3].



(a)



(b)



(c)

Figure 4.4 Scanning Electron Microscope images of (a) Na-BTN, (b) PCH and (c) APPCH.

The results from nitrogen adsorption-desorption (Table 4.1) showed the increasing of specific surface area of porous material (PCH and APPCH) compared with Na-BTN. The results revealed that PCH had the high surface areas of 524.1 m²/g, average pore diameter of 4.85 nm and pore volume of 0.64 cc/g. While the functionalized PCH (APPCH) with amino group (-NH₂) had the decrease of surface area and pore volume compared to PCH and the increasing of APTES content reduced surface area and pore volume. The values of surface area and pore volume were in the range of 119.8-320.5 m²/g and 0.33-0.42 cc/g, respectively. The results indicated that the incorporation of amino group (-NH₂) in porous structure was successful [3, 4, 5].

Table 4.1 Surface area, pore diameters and pore volume from nitrogen adsorption-desorption

Sample	Multipoint BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cc/g)
Na-BTN	31.0	-	-
PCH	524.1	4.85	0.64
APPCH (0.97: 0.03)	320.5	5.21	0.42
APPCH (0.95: 0.05)	275.2	6.04	0.41
APPCH (0.90: 0.10)	119.8	11.12	0.33

Because the observe peak of amino group (-NH₂) in the FTIR is too weak. Thus, the incorporation of organic group (-NH₂) in APPCH was confirmed by CHNS analysis. From the results (Table 4.2), the content of nitrogen and organic molecule (APTES) in APPCH increased with APTES content. The result indicated that the presence of amino group (-NH₂) in the structure of porous clay was successful.

Table 4.2 Element analysis result of APPCH

Sample	N (mg/g sample)	Organic molecule (mmol/g sample)
APPCH (0.97: 0.03)	89.91	0.64
APPCH (0.95: 0.05)	100.07	0.71
APPCH (0.90: 0.10)	141.18	1.01

From the morphology and element analysis results, the APPCH (0.95: 0.05) was selected to modify with pH dye (methyl red) because the high specific surface area of APPCH and the content of organic molecule was sufficient to react with pH dye.

The methyl red adsorption capability of APPCH was observed by calculated the amount of methyl red molecules adsorbed onto the porous samples APPCH compared to PCH as shown in Table 4.3. The result showed that the adsorption

amount of 3.32×10^{-7} mol/ m² of APPCH were higher than the adsorption amount of 1.57×10^{-7} mol/ m² of PCH. The APPCH adsorbed methyl red more than PCH as shown in Figure 4.5. This is caused by the protonation of amino group in APPCH enhanced the electrostatic attraction with methyl red [6].

Table 4.3 Adsorption of methyl red by APPCH and PCH

Sample	Adsorption amount (mol/ m ²)
PCH	1.57×10^{-7}
APPCH (0.95: 0.05)	3.32×10^{-7}

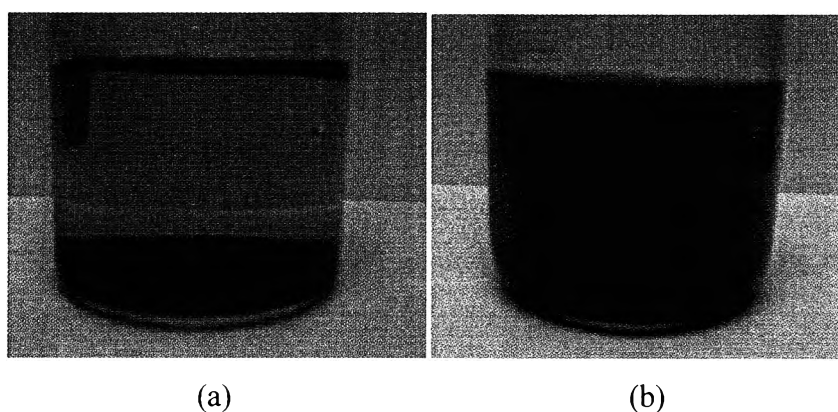


Figure 4.5 Adsorption of methyl red by (a) APPCH and (b) PCH.

B. Characterization of Chromophores Modified APPCH and PCH

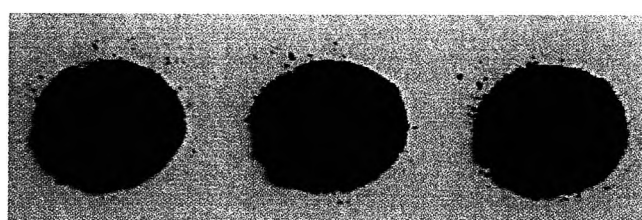
The morphology of the chromophores (methyl red and bromothymol blue) modified APPCH and PCH, respectively was determined by nitrogen adsorption-desorption and the results were reported in Table 4.4. The results showed that the surface area and pore volume of APPCH and PCH decreased while the average pore diameter increased after modification the porous sample with pH dye. The chromophores modified APPCH (APPCH-MR) had the surface area of 69-103 m²/g, average pore diameter in range of 13.10-16.16 nm and pore volume of 0.28-0.34 cc/g. The chromophores modified PCH (PCH-BTB) had the surface area of 32-57 m²/g, average pore diameter in range of 20.12-25.77 nm and pore volume of 0.21-

0.29 cc/g. The results indicated that the results of decreasing of the surface area and pore volume and increasing of pore diameter of APPCH after increasing the pH dye (methyl red) content indicated the presence of dye molecule in the structure of APPCH after modification. The large decrease of surface area and increase of average pore diameter of PCH after modification with pH dye indicated that the large molecule of bromothymol blue incorporated into the structure of PCH and the amount of dye content not have the influence to decrease the surface area.

The chromophores (methyl red and bromothymol blue) modified APPCH and PCH were prepared as shown in Figure 4.6.

Table 4.4 Surface area, pore diameters and pore volume from nitrogen adsorption-desorption

Sample	Multipoint BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cc/g)
APPCH	275.2	6.04	0.41
APPCH-MR (10:1)	69.25	16.16	0.28
APPCH-MR (20:1)	86.79	14.36	0.31
APPCH-MR (30:1)	103.4	13.10	0.34
PCH	524.1	4.85	0.64
PCH-BTB (10:1)	37.73	23.65	0.22
PCH-BTB (20:1)	57.21	20.12	0.29
PCH-BTB (30:1)	32.94	25.77	0.21



10:1

20:1

30:1

(a)

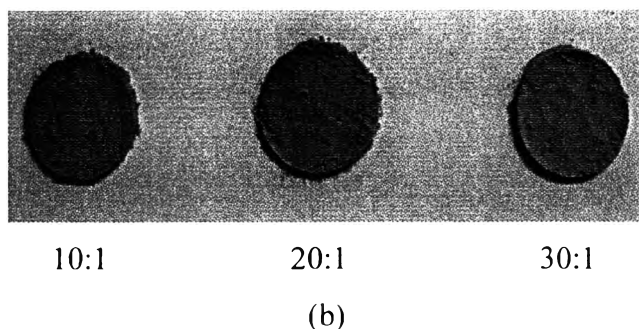


Figure 4.6 (a) methyl red modified APPCH and (b) bromothymol blue modified PCH at various weight ratio of clay and pH dye; 10:1, 20:1 and 30:1.

The XRD patterns of the APPCH and chromophores modified APPCH (APPCH-MR) was shown in Figure 4.7 (a) – (d). The results showed that there was no sharp peak observed in XRD patterns of APPCH and APPCH-MR. A possible reason might be due to the disordered or porous structure of silica framework was formed in the galleries of clay shielding a highly regular interstratification of the clay layer.

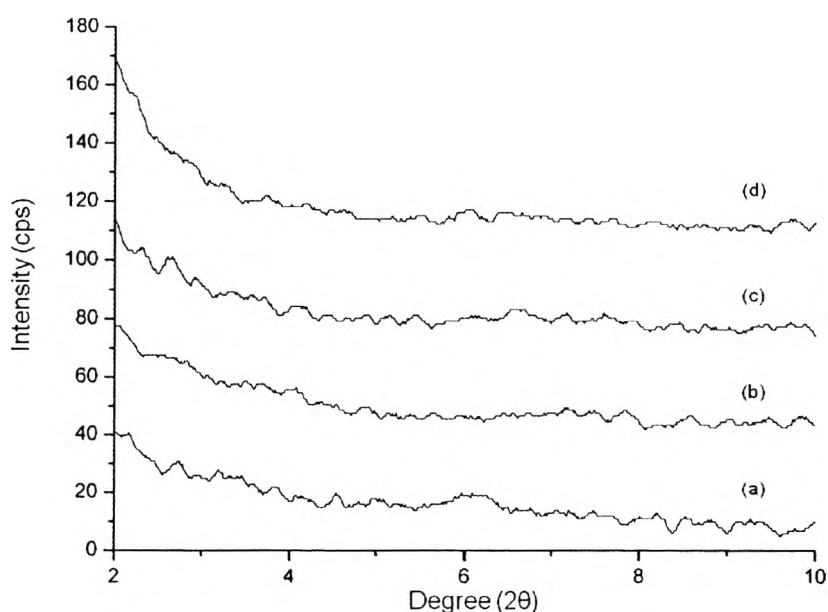


Figure 4.7 The XRD patterns of (a) APPCH, (b) APPCH-MR 10:1, (c) APPCH-MR 20:1 and (d) APPCH-MR 30:1.

The XRD patterns of the PCH and chromophores modified PCH (PCH-BTB) was shown in Figure 4.8 (a) – (d). The results showed that there was no obvious peak observed in XRD patterns of PCH as same as APPCH and APPCH-MR. While the XRD patterns of PCH-BTB showed the peaks around $2\theta = 6.6$ nm which corresponded to the basal spacing about 1.3 nm might be due to the formation of the partial layer structure of PCH after modified with bromothymol blue.

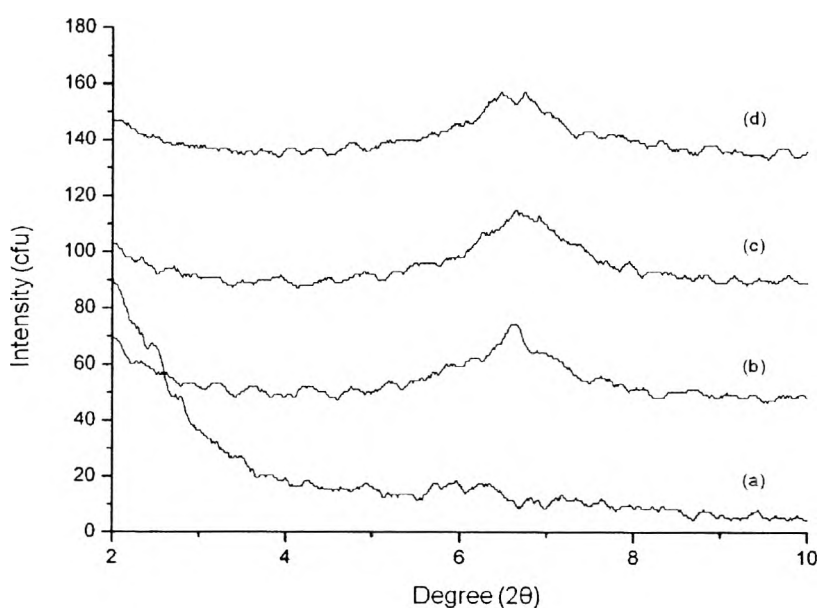
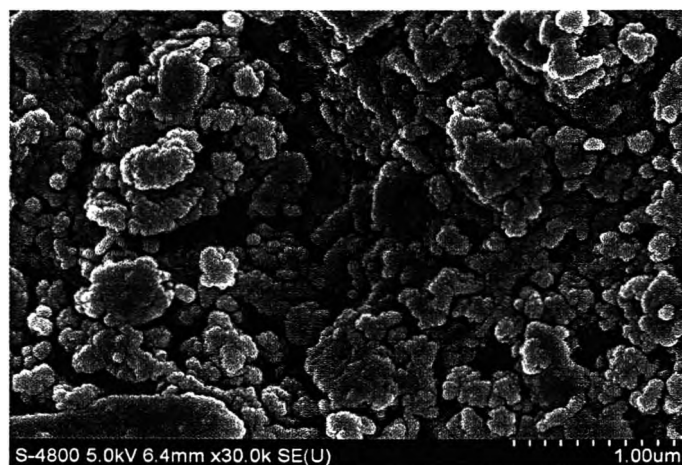
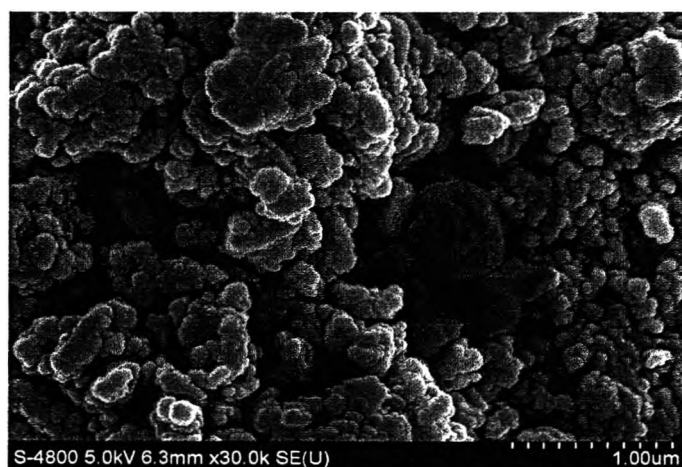


Figure 4.8 The XRD patterns of (a) PCH, (b) PCH-BTB 10:1, (c) PCH-BTB 20:1 and (d) PCH-BTB 30:1

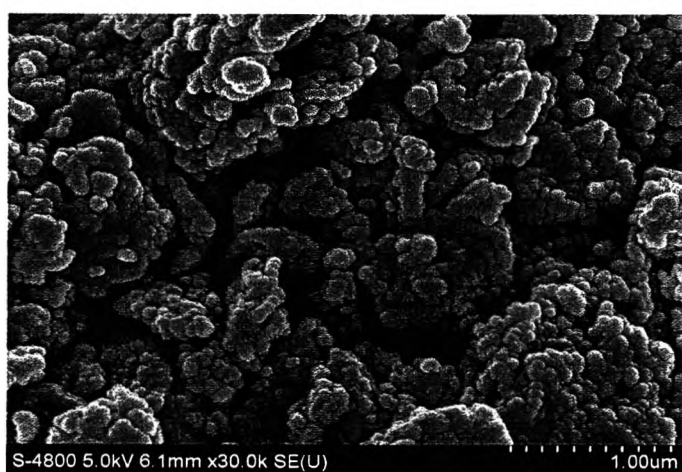
The results of SEM image as shown in Figure 4.9 and 4.10 indicated that the rugged surface of the APPCH and PCH after modified with chromophores (methyl red and bromothymol blue) still remained.



(a)

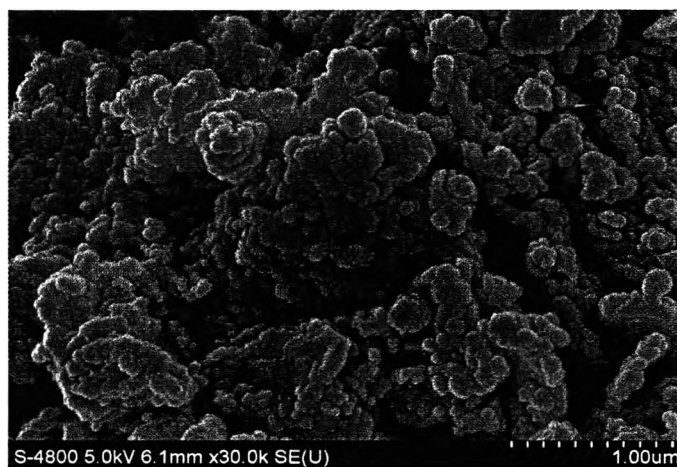


(b)

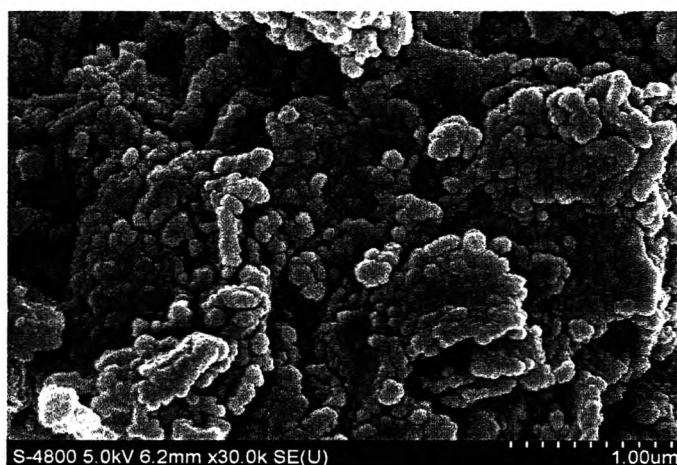


(c)

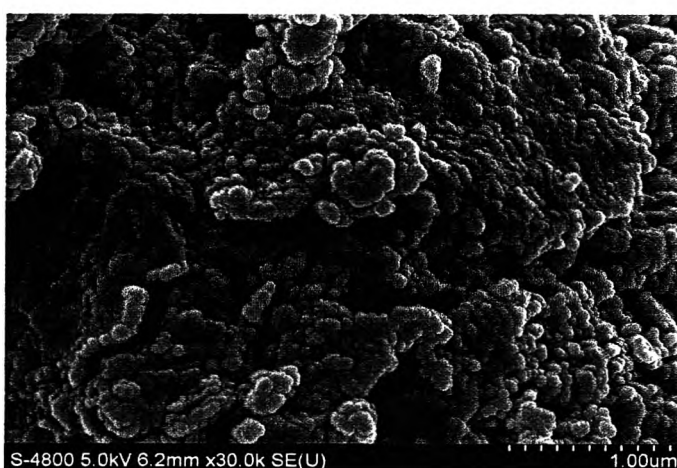
Figure 4.9 SEM images of (a) APPCH-MR 10:1, (b) APPCH-MR 20:1 and (c) APPCH-MR 30:1.



(a)



(b)



(c)

Figure 4.10 SEM images of (a) PCH-BTB 10:1, (b) PCH-BTB 20:1 and (c) PCH-BTB 30:1.

4.5 Conclusions

Porous clay heterostructure (PCH) was synthesized by polymerization of the silica source such as tetraethoxysilane (TEOS) in the presence of surfactant micelles. The obtained functionalized PCH with amino group (-NH₂) was synthesized by co-condensation reaction of TEOS and APTES in order to provide the high selectivity for organic compound. The porous structure of APPCH and PCH was confirmed by N₂ adsorption-desorption, XRD, SEM and FTIR techniques. The incorporated of functional group (-NH₂) into porous material was determined by the increase of nitrogen content in APPCH and the decrease of surface area and pore volume after increasing APTES content. In addition, the incorporation of methyl red in APPCH and bromothymol blue in PCH respectively was confirmed by the decreasing of the surface area and pore volume and increasing of pore diameter of APPCH and PCH after modified with pH dye. Methyl red modified APPCH was aimed to be a sensor for detecting fish freshness. Bromothymol blue modified with PCH can be applied to use as a sensor for detecting the quality of climacteric fruit by color change.

4.6 Acknowledgements

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4.7 References

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