



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Clay Minerals

Bentonite (BTN) was supplied by Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN was 55 mmol/100g of clay.

3.1.2 Surfactants

Cetyltrimethylammonium [$C_{16}H_{33}N^+(CH_3)_3$] bromide was supplied by Fluka. Dodecylamine, $C_{12}H_{27}N$, (98% purified, MW=185.35) was supplied by Aldrich.

3.1.3 Silica Sources

Tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_3$, (MW=208.33) was supplied by Fluka.

3.1.4 Solvents

Methanol (CH_3OH) was supplied by Lab Scan and Hydrochloric acid (HCl) was supplied by Carlo Erba.

3.1.5 Polymer

Poly lactide 4042D (PLA) was supplied by NatureWorks Co., Ltd.

3.1.6 Compatibilizer

Polycaprolactone (PCL) was purchased from Aldrich.

3.1.8 Iron Source

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was supplied by Fluka.

3.2 Equipment

3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay, PCHs 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 2θ range of 1.2-20 degree with scan speed 2 degree/min and scan step 0.01 degree. For the film samples, the experiment was performed on a 10-30 degree with scan speed 5 degree/min and scan step 0.02 degree.

3.2.2 Surface area Analyzer (SAA)

N_2 adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 150°C during 12 h in a vacuum furnace prior to analysis. Surface area 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 wasotherm.

3.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of organoclays, PCHs and Magnetic PCHs were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of $4000\text{-}400\text{ cm}^{-1}$ 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.

3.2.4 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a Perkin-Elmer Pyris Diamond TG/DTA instrument. The clay sample was loaded on the platinum pan and heated from 30°C to 900°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ under N_2 flow of 100 mL/min. For nanocomposites, the sample were heated from 30°C to 500°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ under N_2 flow of 100 mL/min.

3.2.5 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 180°C and cooled down at a rate of 5°C/min under a N₂ atmosphere with a flow rate of 10 ml/min. The sample was then reheated to 200°C at the same rate.

3.2.6 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL JSM-5410 lv Model to observe surface morphology of PCHs. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

3.2.7 Transmission Electron Microscope (TEM)

Transmission electron microscopy performed on JEOL JEM-2100 electron microscope with an accelerating voltage of 160 kV was used to observe the structure of pores. TEM samples were prepared by embedding the powder in resin and sectioning on a ultramicrotome. The thin sections were supported on 300 mesh copper grids.

3.2.8 Gas Permeability Tester

Gas permeation experiments were investigated by Illinois model 8000. The sample films were cut into circular shape with 120 mm in diameter according to ASTM D3985-02. The thickness of the films was 2-3 mm. The films were placed in a desiccator over NaCl and kept for not less than 3 days prior to test.

3.2.9 Twin Screw Extruder

PLA/Magnetic PCHs nanocomposites were prepared using a Collin D-8017 Model T-20 corotating twin-screw extruder with L/D=30 and D=25 mm. The operating temperatures of extruder were maintained at 80, 150, 155, 160, 165, and 160°C from hopper to die, respectively. The screw speed was maintained at 35 rpm.

3.2.10 Compression Molding

The compression molding was performed by using a Wabash V50H Press, at 180°C for 15 minutes and 10 tons compression force for 3 minutes before being cooled down to 50°C.

3.2.11 Gas Chromatography

Gas chromatography with flame ionization detector was utilized to examine ethylene adsorption capacity of the porous clays. Ethylene adsorption was measured by placing each product of 5.00 g 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.

3.2.12 Mechanical Testing

Tensile strength, elongation at break, stiffness and Young's modulus were measured according to ASTM D 882-91 using a LLOYD Mechanical Universal Testing Machine with a 500 N load cell, a 10.00 mm/min crosshead speed and a gauge length 50 mm. Test sample was cut into rectangular shape with a size of 10 mm x 150 mm and thickness in the range of 0.1-0.25 mm.

3.2.13 UV/VIS Spectrophotometer

The absorbance spectra of Magnetic PCHs were 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.

3.2.14 Antimicrobial Activity Testing (The Agar diffusion test)

This method was used to observe antibacteria efficiency that was performed in Luria-Bertani (LB) medium solid agar Petri dish. Starting to inoculate *Escherichia coli* and *Staphylococcus aureus* bacteria into growth medium. Approximately 10^7 colony forming units (CFU) of each microorganism was spread on agar plates. After that, the PCH containing Fe ion was sterilized by autoclaving 15

min at 120°C and then placed on *Escherichia coli*-cultured and *Staphylococcus aureus*-cultured agar plates, which will be then incubated for 24 h at 37°C. The zone of inhibition was measured clear zone and recorded.

3.3 Methodology

3.3.1 Purification and pH Adjustment of Bentonite

Bentonite was pulverized and sieved through 325 mesh. Four 10-g of the passing part were purified by centrifugation and then washed with distilled water several time until pH value was near 7. After that, centrifugation was applied. Again, the same amount of distilled was added, and then the sample was adjusted to pH 9.0 by using dilute HCl and NaOH solutions. The samples were air-dried overnight and pulverized in a mortar.

3.3.2 Synthesis of Porous Clay Heterostructures (PCHs)

The bentonite 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 and study the molar ratio of dodecylamine/TEOS for clay 1 g. The resulting suspension was stirred for further 4 h at room temperature. The solid was separated from solution by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-synthesized PCH 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 mixture of methanol and water and air-dried at room temperature overnight. The PCHs were obtained.

3.3.3 Preparation of Magnetic PCHs

Ferric chloride hexahydrate was used as iron sources which it was added in PCH at 0,5,10,15,20 wt%. Aqueous ammonia was used as the precipitator.

Distilled water was used as the solvent. Before the reaction, N_2 gas was flown through the reaction medium. The reaction was operated in a closed system to provide a nonoxidation environment. NH_4OH was slowly injected into PCH which added ferric chloride hexahydrate under stirring 30 min. The dispersion was centrifuged at 3000 rpm for 20 min. After precipitation, the Fe_3O_4 particles in PCH were repeatedly washed and filtered before drying at room temperature in air atmosphere to form powders.

3.3.4 Preparation of Nanocomposites

1, 2, 3, 4 wt% Magnetic PCHs, 5 wt% PCL and PLA were melt blended in a Model T-20 co-rotating twin-screw extruder (Collin) with $L/D=30$ and $D=25$ mm; the processing conditions were the following: temperature ($^{\circ}C$): 80, 150, 155, 160, 165, and $160^{\circ}C$ from hopper to die, respectively and the screw rotation was 50 rpm. Each composition was premixed in a tumble mixer before introducing into the twin-screw extruder to be well mixed and extruded through a single strand die, and solidified with cold water and pelletized. The obtained pellet was dried in oven.