

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Clay Minerals

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

3.1.2 Surfactants

Cetyltrimethylammonium [$C_{16}H_{33}N^+(CH_3)_3$] bromide was supplied by Fluka.

3.1.3 Co-surfactant

Dodecylamine, $C_{12}H_{27}N$, (98% purified) was supplied by Aldrich.

3.1.4 Silica Sources

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

3.1.5 Solvents

Methanol (CH_3OH) was supplied by Lab Scan, hydrochloric acid (HCl) was supplied by Carlo Erba and ethanol (C_2H_5OH) was supplied by Lab Scan.

3.1.6 Polymer

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

3.1.7 Compatibilizer

Polyethylene glycol (PEG) was supplied by Sigma.

3.1.8 Iron Source

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) was supplied by Fluka.

3.1.9 Manganese Source

Manganese (II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) was supplied by Fluka.

3.1.10 Vapor Corrosion Inhibitor

VCI 609 was provided by Optimal Technology Co., Ltd.

3.2 Equipments

3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay and PCH 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 1.2-20 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 15 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.

3.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of montmorillonite, organoclays, PCH, Magnetic Clay and nanocomposites film 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.

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°C/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°C/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 PCH. 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 and the dispersion of PCH in polymer matrix of nanocomposites. 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 X-Ray Fluorescence Spectrometer (XRF)

X-Ray Fluorescence Spectrometer (XRF) was used to observe the chemical composition of PCH and magnetic PCH. XRF analyses were carried out using a Phillips PW2400 and Oxford ED-2000 instrument.

3.2.9 Gas Permeability Tester

Gas permeation experiments were investigated by Brugger Gas Permeability Tester. The sample films were cut into circular shape with 110 mm in diameter according to ASTM 1434-82. The thickness of the films was measured with the peacock digital thickness gauge model PDN 12N by reading ten points at random position over the entire test area and the results were averaged. The films were placed in a desiccator over NaCl and kept for not less than 3 days prior to test.

3.2.10 Water vapor Permeability Tester

Water vapor permeability was investigated according to Water Vapor Transmission Rate-Dish Method ASTM E 96

3.2.11 Atomic Force Microscope (AFM)

Atomic force microscope performed on XE-Series Park Systems SPM Controller with non-contact mode, scan size 40 μm . and scan rate 0.3 Hz. was used to observe the surface of carbon steel.

3.2.12 Vibration Sample Magnetometer (VSM)

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

3.2.13 The Volatilization of VCI Test

The volatilization of VCI test was investigated the volatilization of VCI in the porous clays. The sample was placed in a jar about 15 g, with an airtight lid holding the litmus paper.

3.1.14 The Corrosion Test

Corrosion Test was investigated according to the Federal Standard No.101C, Method 4031 with a few modifications. For powder sample, the carbon steel test specimens were polished with the emery paper, in order to eliminate heterogeneities. The chamber was a glass jar containing 45 ml of water/glycerin solution, with an airtight lid holding the carbon steel specimens, and a sample pan containing 1 g of pure VCI and porous clays which was modified by VCI, and then the sample pan was placed at the bottom of the jar on the water surface. For film sample, the carbon steel test specimens were polished with the emery paper and were inserted in sealed film packages, and then submitted to further corrosion test.

3.2.15 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 x 150 mm and thickness in the range of 0.1-0.25 mm.

3.2.16 UV/vis Spectrophotometer

The absorbance spectra of Magnetic clay 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.

3.2.17 Twin Screw Extruder

PLA/Clay nanocomposites were prepared using a Labtech Engineering corotating twin-screw extruder with L/D=40/1 and D=20 mm. The operating temperatures of extruder were maintained at 80, 150, 160, 160, 160, 160,170,170,170 and 175°C from hopper to die, respectively. The screw speed was maintained at 50 rpm.

3.2.18 Compression Molding

The compression molding was performed by using a Wabash V50H Press, at 185°C for 10 minutes and 27 tons compression force for 15 minutes before being cooled down to 50°C.

3.3 **Methodology**

3.3.1 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.

3.3.2 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.

3.3.3 Preparation of Magnetic PCH

Ferric chloride hexahydrate and ferrous chloride tetrahydrate were used as iron sources which they were added in PCH at 20 wt%. Manganese (II) chloride tetrahydrate was used as manganese sources which it was added in PCH at 5, 10, 15 and 20 wt%. Aqueous ammonia was used as the precipitator. Distilled water was 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 Fe₂O₃ particles in PCH were repeatedly washed and filtered before drying at room temperature in air atmosphere to form powders.

3.3.4 Preparation of Magnetic PCH-VCI

Vapor corrosion inhibitor was add in magnetic PCH at 20, 40, 60 and 80 wt% and stirred in ethanol which is used as the solvent at 50 °C for 30 min. The reaction was operated in a closed system to protect a volatility of VCI. After the reaction time, the solid was filtered out, washed with a mixture of methanol and water and then air-dried to form powders.

3.3.5 Preparation of Nanocomposites

1, 2, 3, 4 and 5 wt% Magnetic PCH-40%wt VCI, 5 wt% PEG and PLA were melt blended in a co-rotating twin-screw extruder (Lab tech) with L/D=40/1 and D=20 mm; the processing conditions were the following: temperature (°C): 80, 150, 150, 160, 160, 165, 165, 170, 170 and 175°C from hopper to die, respectively and the screw rotation is 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 before compression molding.