



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Monomer

Divinylbenzene (DVB) was supplied by Merck.

3.1.2 Solvents

Toluene (T) and Hydrochloric acid (HCl) were supplied by Lab Scan. Ethanol (EtOH) was supplied by Carlo Erba. Isopropanol was supplied by Etalma.

3.1.3 Surfactants

Sorbitan monooleate (SPAN80) and Dodecylbenzenesulfonic acid, sodium salt (DDBSS) were supplied by Sigma. Cetyltrimethylammonium $[C_{16}H_{31}N^+(CH_3)_3]$ bromide (CTAB) and 2,5-dimethoxy-4-(n)-amylamphetamine (DOAM) were supplied by Fluka.

3.1.4 Clay Minerals

Bentonite (BN) was supplied by Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43 mmol/100g of clay.

3.1.5 Initiator

Potassium persulfate ($K_2S_2O_8$) was supplied by Fluka.

3.1.6 Stabilizer

Calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) 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, and acid-treated clay and to investigate the crystal structure of nanocomposites. X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered $Cu K_{\alpha}$ radiation operated at 40 kV and 30 mA. The powder samples were observed on the 2θ range of 1.8-20 degree with scan speed 2 degree/min and scan step of 0.02 degree.

3.2.2 Surface Area Analyzer (SAA)

N₂ adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 100°C during 12 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 organoclays and acid-treated clay 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)

Thermo-gravimetric analysis (TGA) was performed to measure the thermal stability of the poly(DVB)HIPEs. TGA of both neat and poly(DVB)HIPE nanocomposites were performed using a Mettler Toledo TGA/SDTA 851e instrument. Experiments were carried out under nitrogen gas atmosphere. Samples were cut into small pieces weigh about 2–5 mg. Then the samples were loaded on the platinum pan and heated to 600°C from 40°C at a heating rate of 10°C/min. One steps degradation was observed during testing, and the decomposition temperature was recorded corresponding to 50% decomposition of the material.

3.2.5 Differential Scanning Calorimetry (DSC)

The glass transition temperature of poly(DVB)HIPEs was determined using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 250°C and cooled down at a rate of 10°C/min under a N₂ atmosphere with a flow rate of 10 mL/min. The sample was then reheated to 250°C at the same rate.

3.2.6 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL/JSM 5200 Model to observe surface morphology of poly(DVB)HIPEs. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

3.2.7 X-ray Fluorescence (XRF)

Chemical compositions of organo clay and acid-treated clay were obtained using Oxford Model ED2000 X-ray tube with silver as a filter, operate at voltage 35 kV.

3.2.8 Transmission Electron Microscope (TEM)

Transmission electron microscopy was also used in this studied to observe the morphology of the poly(DVB)HIPE nanocomposites. TEM micrographs were taken on a Tecnai G2 Sphera electron microscope with an accelerating voltage of 80 kV to observe the pore structure and secondary pore in the cell wall of poly(DVB)HIPEs. Micrographs were recorded at magnifications of 80000 \times and 150000 \times magnification. TEM samples were prepared by embedding polyHIPE nanocomposites in a support resin and sectioning on an ultra-thin microtome. The thin sections were supported on 300 mesh copper grids.

3.2.9 Universal Testing Machine (LLOYD)

A Lloyds Universal Testing Machine (Lloyds/LRX) equipped with a 500 N load cell was used to measure mechanical properties in compression. The samples were loaded at a rate of 1.27 mm/min. Samples of 25.4 mm in diameter and 25.4 mm in height were used for tested of each poly(DVB)HIPEs. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached.

3.2.10 CO₂ Gas Adsorption

Study of CO₂ gas adsorption capacities of poly(DVB)HIPE filled with acid-treated clay were carried out using a pilot gasification unit at the Chemical Technology Department, Faculty of Science, Chulalongkorn university. Samples were cut into small pieces weigh about 1–2 g. Then the samples were loaded into sample tube 2 \times 25 cm. CO₂ 3 mL/min and He 17 mL/min were flowed through the sample at room temperature. The residue of CO₂ was measured by a Gas Chromatography instrument, column used Shimadzu 2014, flow rate 35 mL/min.

3.3 Methodology

3.3.1 Preparation of Acid-treated Clay

Na-bentonite clay was slowly added to 3N HCl solutions, stirred and maintained at 110°C for 3 h. The clay/acid ratio used in the study was 2% wt/wt. After treatment, the clay was separated and washed with distilled water several times and dry until constant weight was obtained and grind. 1g of the obtained acid-treated clay was added to 30 mL of distilled water and stirred at 80°C for 24 h. 3.78 g of DOAM, 15 mL of EtOH, and 15 mL of H₂O were added to acid-treated clay solution for modified clay. Then stirred solution for 3 h until transparent, added warm water and filtered, and washed by soxhlet overnight with ethanol (Venaruzzo *et al.*, 2002).

3.3.2 Preparation of Poly(DVB)HIPE filled with Acid-treated Clay

The cellular materials were prepared by first dissolving organic phase containing 5 mL of DVB monomer, 5 mL of toluene, required amounts of acid-treated clay, and a mixture of nonionic, anionic, and cationic surfactants: SPAN80, DDBSS, and CTAB was added to the mixture, stirred for 10 min. While 90 mL of distilled water containing 0.2 g of potassium persulfate and 1 g of calcium chloride dihydrate were added dropwise. After all the water has been added, the emulsion was further stirred for 20 min and placed in a glass bottle. The obtained emulsions were capped and put in a convection oven at 70°C for 48 h to polymerize (Barbetta *et al.*, 2004). After polymerization, the cellular materials were removed from the glass bottles and washed by soxhlet for 6 h with 2-propanol. Then the cellular materials were returned to vacuum oven to dry at 80°C for 48 h (Pakeyangkoon *et al.*, 2008).

3.3.3 Characteristics of Acid-treated Clay and Poly(DVB)HIPEs filled Acid-treated Clay:

- a. Thermal properties characterizing: The thermal properties of poly(DVB)HIPEs filled with acid-treated clay were studied using TGA and DSC.
- b. Morphology characterizing: The morphology of poly(DVB)HIPEs filled with acid-treated clay was studied using SEM and TEM.
- c. Structural characterizing: The structural characteristics of acid-treated clay were measured using XRD and FTIR.

- d. Chemical characterizing: The chemical analyses of acid-treated clay were carried out using XRF.
- e. Mechanical properties analysis: The mechanical properties of poly(DVB)HIPEs filled with acid-treated clay were studied using LLOYD/LRX.
- f. Surface area analysis: The surface area of poly(DVB)HIPEs filled with acid-treated clay was analyzed using Autosorb-1.
- g. Adsorption analysis: Study of toxic gases adsorption properties of poly(DVB) HIPE filled with acid-treated clay were carried out using a pilot gasification unit at the Faculty of Chemical Technology Chulalongkorn university.