CHAPTER III
EXPERIMENTAL

3.1 Materials

Pyrrole of 97% purity was purchased from Merck. Iron (III) chloride $FeCl_3.6H_2O$, a product of Fluka, was used as an oxidizing agent. Sodium montmorillonite (Na-MMT) with cation exchange capacity of 119 meq/100g was supplied by Kunimine Industrial Co., Ltd., Japan. Dodecylbenzenesulfonic acid sodium salt, a product of Fluka, was used as a doping agent. Octadecylamine (OC) for modification of Na-MMT was obtained from Fluka.

The chemical structure of octadecylamine was shown in Figure 3.1

Octadecylamine (OC)

Figure 3.1 Chemical structure of octadecylamine (modifying agents).

3.2 Experimental Equipment

3.2.1 Fourier-Transform Infared Spectrometer (FT-IR)

FT-IR was used to determine functional groups of organic substances. The spectra were obtained from a BRUKER Equinox 55 spectrometer, using 16 scans at a resolution of 4 cm^{-1}. A deuteriated triglycinesulfate detector (DTGS) with a specific detectivity, D*, of $1x10^9$ $cm.Hz^{1/2}.W^{-1}$ was used to measure intensities within the frequency range of 4000-400 cm^{-1}. KBr pellet technique was applied in the preparation of the analyze samples.

3.2.2 Wide-angle X-ray Diffractometer (WAXS)

XRD spectra were recorded by using a D/MAX-2000 series Rigaku/X-ray Diffractometer that provides X-ray of Cu K-alpha at 40 kV/30 mA. The glass sample holders were employed for all the samples. The experiment was operated in the 2θ range of 2-30 degree at the scan speed of 5 degrees/min and 0.02 degree of scan step.

3.2.3 Thermogravimetric Analyzer (TGA)

A DuPont TGA 2950 was employed to observe degradation temperature of materials used. The chamber was continuously flushed separately with both nitrogen gas and oxygen gas at the flow rate of 20 mL/min. The temperature range used was between 30-800°C for a modifying agent and the clay and was between room temperature to 650°C for pure PPy and the nanocomposites. The heating rate was set at 10°C/min.

3.2.4 Keithley Electrometer (Model 6517)

Resistance of samples was measured by using a Keithley Electrometer Model 6517. Under ambient air atmosphere, an AC voltage of 10 volts was applied for 60 seconds and the resulting resistance was then measured. For measuring resistance of samples under CO_2, CH_4, C_2H_4 atmosphere, the pressure of gas was set at 0.1 bar and an AC voltage was applied at 10 volts. The resulting resistance was then measured with time up to 300 seconds. The samples were prepared in the pellet form using Hydraulic Press, GRASEBY SPECAC (8 bars pressure for 2 min).

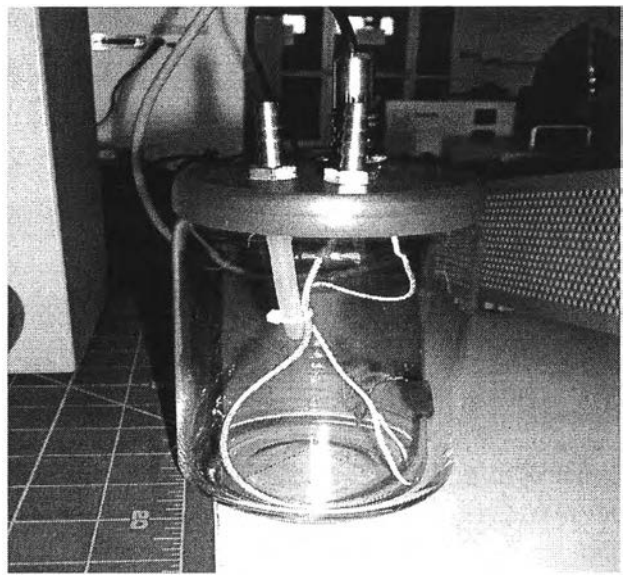

Figure 3.2 Electrode of resistance chamber.

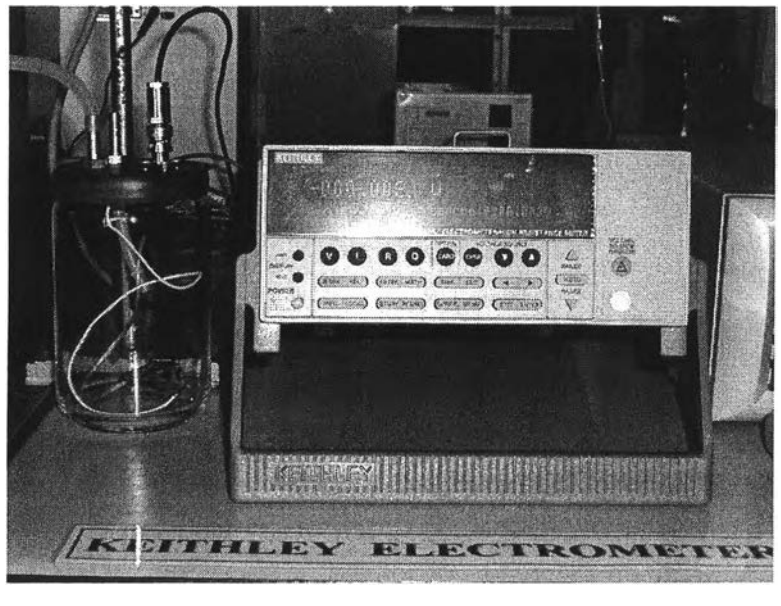

Figure 3.3 Keithley Electrometer (Model 6510) for resistance measurement.

The cross sensitivity of the samples was calculated by the following equations:

$$\text{Cross sensitivity for } R_1 = \frac{R_{1+2}}{R_1} \qquad (3.1)$$

and

$$\text{Cross sensitivity for } R_2 = \frac{R_{1+2}}{R_2} \qquad (3.2)$$

where:

R_{1+2} = resistance of sample sensor to the mixture of gas 1 and gas 2

R_1 = resistance of sample sensor to gas 1

R_2 = resistance of sample sensor to gas 2

3.3 Experimental Methods

3.3.1 Purification of Pyrrole

Pyrrole (97%, Merck) was purified by vacuum distillation and stored in a dark glass bottle in a refrigerator at about 4°C before using.

3.3.2 Preparation of Organically Modified Montmorillonite

The octadecylammonium-montmorillonite (OC-MMT), an organically modified montmorillonite, was synthesized by an ion exchange reaction between Na-MMT and octadecylamine (OC). Na-MMT (10 g) was stirred in 300 ml distilled water for 2 hours and heated at 80°C for half an hour. At the same time, a solution of 1.5 equivalent of OC and 3 equivalent of HCl was heated at 80°C for half an hour to give an octadecylammonium solution. The alkylammonium solution was then added with vigorous stirring

to the Na-MMT suspension and kept at 80°C for 2 hours. OC-MMT was separated by filtration, rinsed with 2L of hot distilled water. The product was dried overnight at 80°C, ground with a centrifugal ball mill, and kept in a bottle (Ratanarat *et al.*, 2003). A diagram of the preparation of organically modified montmorillonite is shown in Figure 3.4.

3.3.3 Synthesis of Polypyrrole

Polypyrrole was chemically synthesized in 50 mL distilled water by mixing a 0.043 mole (2.881g) of pyrrole solution with a 0.1 mole (27.03 g) of an oxidizing solution of $FeCl_3$ (molar ratio of FeCl3/pyrrole = 2.3:1). The pyrrole solution was kept in the bath before adding $FeCl_3$ and the addition was done slowly at low temperature due to a highly exothermic reaction. The synthesis was allowed to proceed at 5-7°C for one hour. The precipitate polypyrrole was collected by filtration, rinsed with distilled water and dried in a vacuum oven at 35°C (Ramelow *et al.*, 2001).

3.3.4 Preparation of PPy/OC-MMT Nanocomposites

Polypyrrole-layered silicate nanocomposites (PPyC) were synthesized by mixing 1, 3, 6, and 9% weight of OC-MMT with pyrrole at room temperature. The pyrrole/OC-MMT mixture was cooled in a bath with slow stirring at 5-7°C followed by slowly adding $FeCl_3$ solution. The synthesis was performed in one hour. The resulting product was collected by filtration, rinsed with distilled water and dried in a vacuum oven at 35°C.

3.3.5 Preparation of DBSA-doped PPy/OC-MMT Nanocomposite

DBSA-doped polypyrrole-layered silicate nanocomposite (DPPyC) was prepared by stirring PPyC3 (3% by weight of OC-MMT) in a solution of DBSA for one hour. The DBSA solution was obtained by dissolving DBSA (7.4836 g) in 50 mL distilled water. The PPy:DBSA mixture molar ratio was 1:0.5; H^+/PhN = 0.5 (Moon *et al.*, 1999). At the end of the

reaction, the product was collected by filtration, rinsed with distilled water and dried in a vacuum oven at 35°C.

Table 3.1 Compositions of PPy/OC-MMT nanocomposites.

Sample	Pyrrole (g)	OC-MMT (g)	wt% OC-MMT	DBSA (g)
PPyC1[a]	2.8881	0.0291	1	-
PPyC3	2.8881	0.0891	3	-
PPyC6	2.8881	0.1389	6	-
PPyC9	2.8881	0.2849	9	-
DPPyC3	2.8881	0.0891	3	7.4836
nDPPyC3	2.8881	0.0891	3	14.9772

[a]Number at the end of acronym indicates wt% of OC-MMT in the nanocomposites.

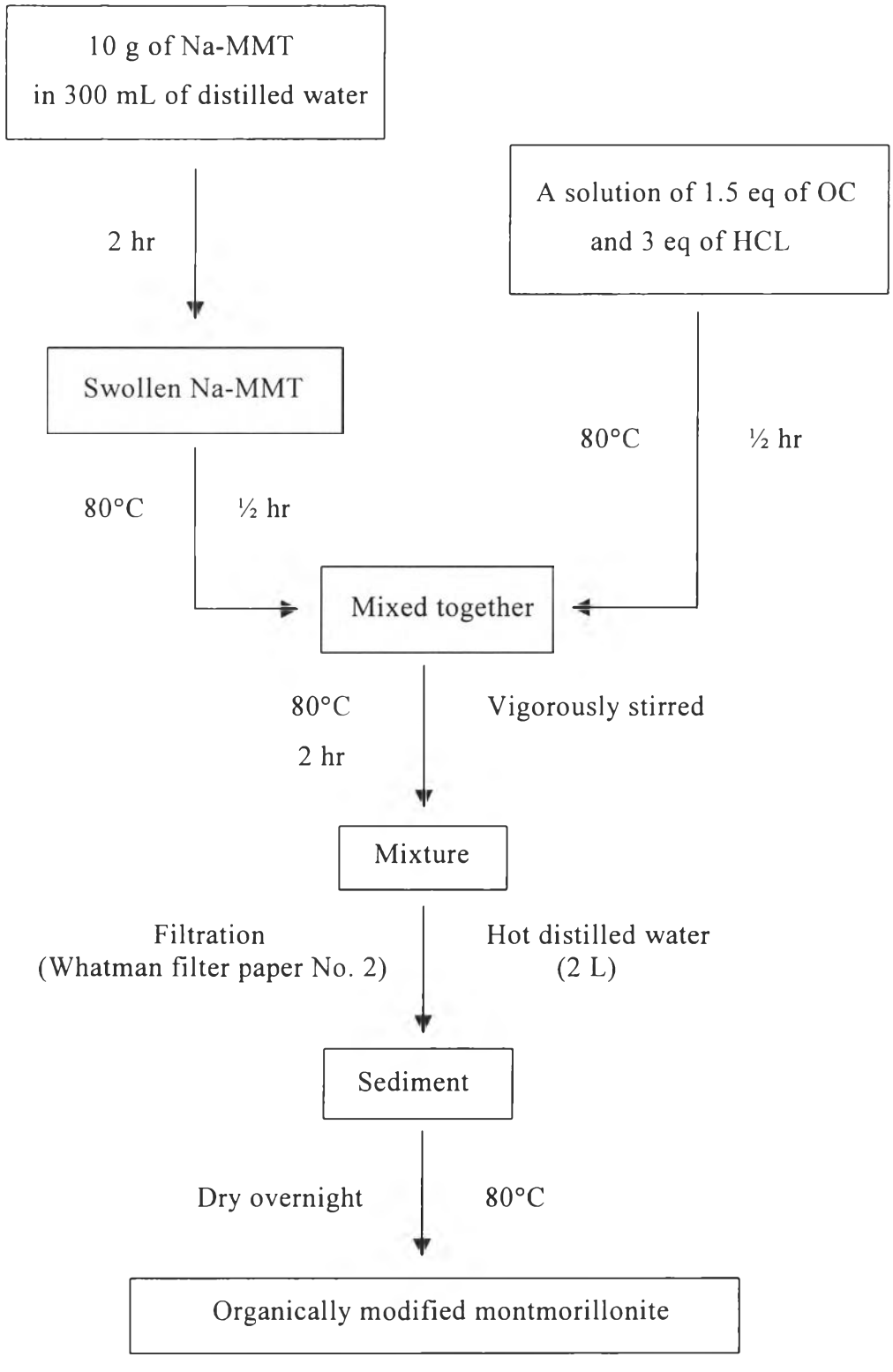

Figure 3.4 A diagram of the preparation of organically modified montmorillonite.