



CHAPTER III EXPERIMENTAL SECTION

3.1 Materials

Bisphenol-A, n-butylamine, 6-aminocaproic acid, 2,4,5-trimethyl aniline, 4-amino-N,N-dimethyl aniline dihydrochloride and p-phenetidine were purchased from Fluka Chemical, Switzerland. Thin layer chromatography (TLC) sheet and dodecylamine were supplied by Merck. Dioxane (AR grade) was purchased from Carlo Erba. Paraformaldehyde was purchased from Sigma Chemical. All of chemical were used without further purification. The chemical structures of some chemical reagent are shown in Figure 3.1.

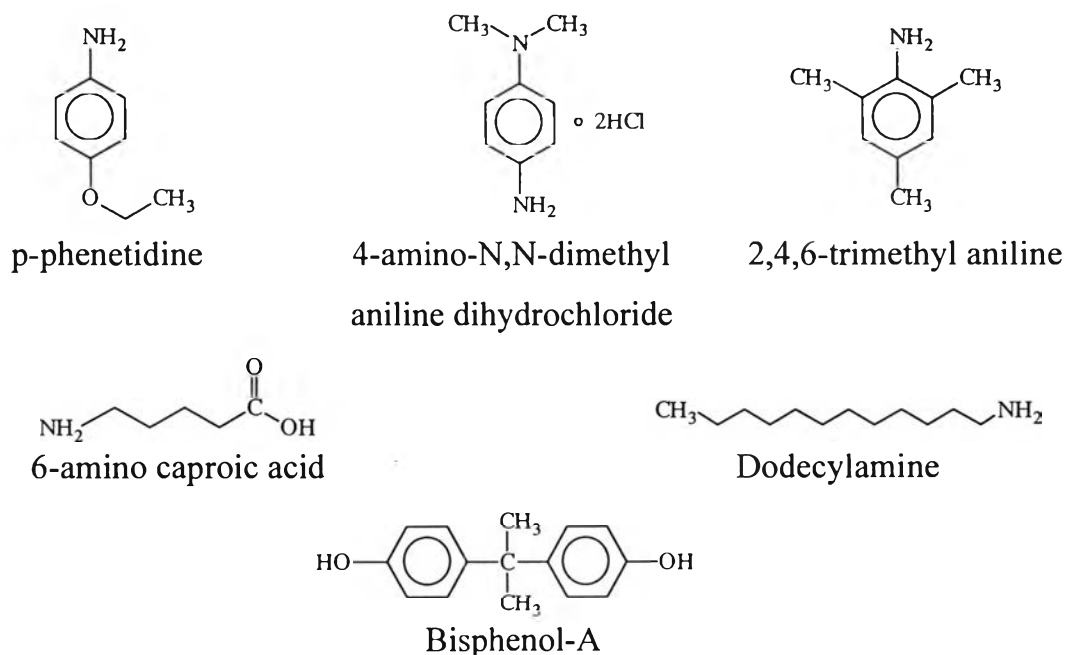


Figure 3.1 Chemical structures of the modifying agent and bisphenol-A.

Sodium-montmorillonite with cation exchange capacity (CEC) of 119 meq/100g was supplied by Kunimine Industrial Co., Ltd., Japan.

3.2 Equipment

3.2.1 Thermogravimetric Analysis (TGA)

TGA thermograms were obtained from Perkin Elmer TGA 7. The chamber inside the analyzer was exposed to a continuous flow of nitrogen at flow rate of 20 ml/min and a protective purge gas for balance unit was at flow rate of 30 ml/min. The temperature program was started at 50 °C to 900 °C with a rate of 10 °C/min.

3.2.2 Differential Scanning Calorimeter (DSC)

DSC data were obtained from 910S differential scanning calorimeter TA instrument of Dupont. Three to five mg of sample was filled in hermetic sample pan with the pin hold on the lid. The experiment was run in the non-isothermal mode from 30 °C to 300 °C with scanning rate 20 °C/min.

3.2.3 Fourier Transform Infrared Spectrophotometer (FTIR)

FTIR spectra were obtained on a VECTOR 3.0 BRUKER spectrometer with 32 scans at a resolution of 2 cm⁻¹. A frequency range of 4000-400 cm⁻¹ was observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D*, of 1x10⁹ cmxHz^{1/2}xW⁻¹. Both neat techniques on ZnSe plate and KBr pellet were used.

3.2.4 Size Exclusion Chromatography (SEC)

SEC chromatograms were performed by water GPC 600E attached with IR and UV detectors (Waters 410 and 486, respectively). The separating columns were HR0.5 and HR1, which could separate the molecular weight species from 50-1000 and 100-5000 respectively. The absorbance at 254 nm was used for determination of benzoxazine by UV detector.

3.2.5 Atomic Absorption Spectrophotometer (AAS)

The % ion exchange was determined by an atomic absorption spectrometer Varian SpectrAA-300 that acetylene is used as fuel and air is used as supported gas. The hollow cathode lamps used are sodium cathode lamps for sodium ion with 5 mA lamp current. Ion solution standard 1000 ppm was prepared according to the analytical method of Varian. The wavelength at 589.0 nm was used to determine the absorbance of sodium ion. The standard curve was prepared and shown in Appendix I.

3.2.6 Wide Angle X-ray Diffractometer (WAXD)

WAXD spectra were obtained from D/MAX-2000 series of Rigaku/X-ray Diffractometer system. X-ray of Cu K-alpha at 40 kV/ 30mA was used as source. Thirty eight μm of pulverized samples and composite films were filled in the standard sample holder. K-beta filter was used to eliminate interference peak. Divergence slit and scattering slit at 1 deg together with 0.3 mm of receiving slit were set on the instrument. The experiment was performed in the range of 2-30 degree with scan speed 5 deg/min and scan step 0.02 deg.

3.2.7 Transmission Electron Microscope (TEM)

A small piece of sample film (0.5×0.5 mm) was embedded in the spurr resin and fumed in oven at 70°C for 8 hrs. This sample in the resin was cut by ultra microtome. The sample with 90 nm thickness was picked up from the water surface and placed on a copper supporting grid and stained with 2% OsO_4 vapor for 2 hours to enhance the phase contrast of the images. The micrographs were produced using a JEOL electron Microscope, model JEM-200CX, with an acceleration voltage of 120 kV. The magnification of all images was adjusted in the range of 1000 to 73000 X.

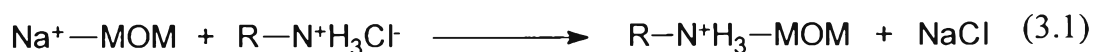
3.3 Methodology

3.3.1 Preparation of Benzoxazine Monomer

The synthesis procedure was as following: the mixture of 0.4 mole paraformaldehyde dissolved in 80 ml dioxane were poured in 500 ml three-necked flask equipped with thermometer, condensor and dropping funnel. It was cooled by ice bath; then 0.2 mole n-butylamine in 20 ml dioxane was added slowly and temperature was kept below 10 °C. The mixture was stirred magnetically for 10 min before adding the solution of 0.1 mole bisphenol-A in 100 ml dioxane and the temperature was rised up for refluxing. Thin layer chromatography used for reaction checking was performed with 1:1 ratio of ethyl acetate:chloroform as a mobile phase. The solvent was removed in rotatory evaporator machine and viscous fluid was dissolved in 200 ml ethyl ether. This ether solution was washed with 3 N NaOH for 3 times or until the NaOH layer was colorless. Then ether solution was washed with water for 3 times and dried with sodium sulfate anhydrous. Evaporating the ether resulted to obtain a viscous fluid at room temperature. A diagram of preparation method is shown in Figure 3.2.

3.3.2 Preparation of Organically Modified Na⁺-Montmorillonite (OMOM)

The organically modified silicate layer of Na⁺-Montmorillonite was expectedly prepared by ion-exchange reaction between Na⁺-Montmorillonite and protonated form of amine as shown in eq. (3.1).



Ten g of Na⁺-Montmorillonite was stirred in 175 ml distilled water at room temperature overnight. Separated solutions of excess amine

(2xCEC) with respect to montmorillonite amount and excess concentrated HCl with respect to amine in 50 ml distilled water were heated to 80 °C. The protonated amine solution was added slowly to montmorillonite suspension and then kept at 80 °C. After mixing, the volume of suspension was increased to 400 ml and stirred at 80 °C for 12 hr. The organically modified montmorillonite (OMOM) was recovered by filtering and washing this sediment with 3 lit of 80 °C distilled water. The final product was dried at 100 °C in vacuum oven. The product was pulverized with mortar and sieved with 38 micron mesh size. The amine that used as the modifying agent in this work consisted of dodecylamine (DODEC), 6-aminocaproic acid (CAPRO), 4-amino-N,N-dimethyl aniline dihydrochloride (ANDAD), p-phenetidine (PHEN) and 2,4,6-trimethylaniline (TMAN). Their chemical structures were shown in the Figure 3.1.

3.3.3 Study of Swelling of OMOM in Various Type Solvent

Study of swelling of OMOM was performed for selection of the best solvent used for preparation of composite material. Two hundreds mg (with ± 1 mg error) of OMOM was weighed in the 5 ml measuring cylinder and then 5 ml of organic solvent was added into the measuring cylinder. The cylinder was shaken and left it for 24 hr. The volume of swelling of OMOM were recorded and the cylinder was shaken and left again to confirm the equilibrium of swelling. Types of organic solvents used in this work were dioxane, toluene, methanol, ethanol, n-propanol and iso-propanol. Moreover, the binary solvent systems of 5, 10, 15, 25 % vol./vol. of methanol in toluene were studied.

3.3.4 Preparation of Nanocomposite

The preparations of 3% by weight of OMOM in polybenzoxazine composites (PBC) were synthesized with mono solvent, binary solvent and

non-solvent system. When solvent was used, OMOM was dispersed in the solvent (10 times by weight of OMOM) at room temperature for 1 hr, and mixed with an added solution of 7 g benzoxazine monomer and 5 ml dioxane at 50 °C. The mixture was stirred at 1000 rpm and samples were collected every 2, 4 and 6 hour. All samples were casted on aluminum foil surface and solvent was evaporated in a vacuum oven at 100 °C for 2.5 hr. Curing was performed under ambient condition in furnace at 230 °C for 90 min.

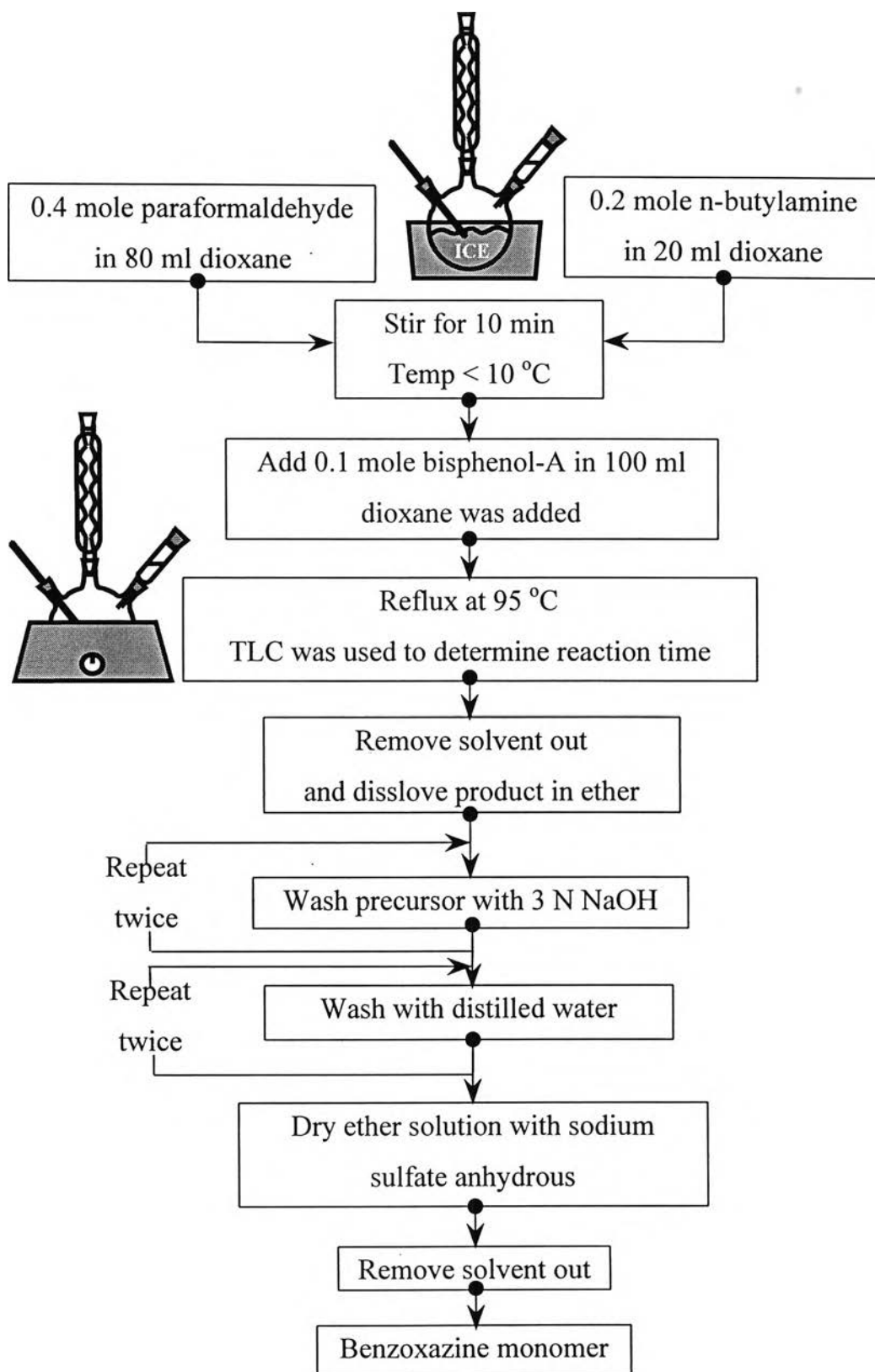


Figure 3.2 A diagram of preparation of benzoxazine.

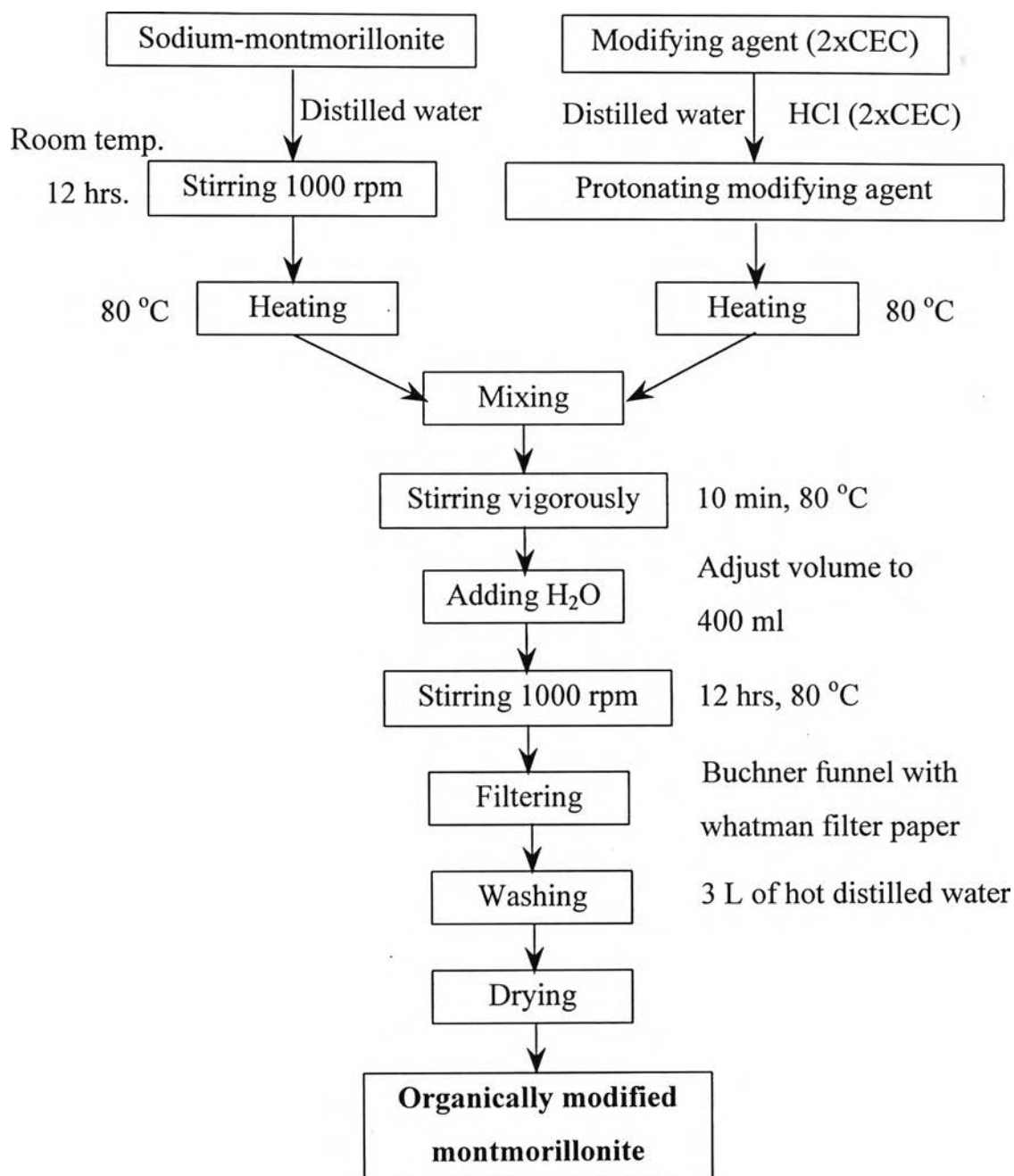


Figure 3.3 A diagram of preparation method of organically modified montmorillonite.