

CHAPTER III EXPERIMENTAL

3.1 Materials

All chemicals were used without further purification. Polybenzoxazine precursor was synthesized using 4,4'-methylenedianiline ($\geq 97\%$) which purchased from Fluka Co., Ltd, Formaldehyde (37%wt. in water) was obtained from Merk Shap & Dohme Cooperation company and Phenol detached crystals (99.99%) was obtained from Fisher Chemical company. *N, N*, -dimethylformamide was used as solvent and purchased from RCI Labscan Co., Ltd. Hexadecyltrimethylammonium bromide (96%) was used as surfactant to stabilize the sol-gel structure obtained from Fluka Co., Ltd.

3.2 Measurements

The functional groups related to structure of materials were investigated by using FTIR technique. The FT-IR spectra were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 400-4000 cm^{-1} with 64 scans at a resolution of 2 cm^{-1} . KBr pellet technique was applied in the preparation of powder samples. The carbon, hydrogen, nitrogen and sulfur weight percentages of samples were investigated using a Vario EL III elemental analyzer. DSC analyzer was carried out using a Perkin-Elmer DSC 7 instrument. The sample was heated from 25 to 300 °C with heating rate 10 °C per minute under N_2 atmosphere with flow rate 20 ml per minute. Finally, the heating profile, curing temperature and completely cured polybenzoxazine were obtained. TGA instrument was also conducted with Perkin Elmer Thermogravimetric /Differential Thermal Analyzer (TG-DTA). The sample was loaded in rang 4-8 mg on the alumina pan and heated from 50 to 900 °C under nitrogen atmosphere with flow rate 50 ml per minute and heating rate 10 °C per minute. The pyrolyzed temperature of polybenzoxazine was investigated from the onset temperature whereas char yield as the weight residue at 800 °C was reported. The X-

ray powder diffraction pattern of the carbon foam was obtained using an XRD (Bruker AXS D8 ADVANCE) spectrometer with Cu K α irradiation ($\lambda = 0.15406$ nm) at 40 kV and 30mA to examine the graphitization of the carbon xerogel after carbonization. X-ray photoelectron spectroscopy (XPS) used to investigate the changing structure carbon at different pyrolysis temperature. X-ray photoelectron spectroscopy, XPS (Kratos Axis Ultra DLD) was used to determine the oxidation states of carbon xerogels. A monochromatic AlK α was used as an X-ray source (anode HT = 15 kV). The residual pressure in the ion-pumped analysis chamber was lower than 5×10^{-7} torr. The binding energies were referenced to the O1s peak (529.2 eV) to account for the effects of charging. Raman spectra were recorded with a Sen-terra Dispersive Raman Microscope (Bruker Optics) using laser excitation wavelength at 532 nm with a TE-Cooled CCD detector. The electrical conductivity values of the carbon xerogels were obtained by a custom-buit two-point probe. A conductivity meter (Keithley 6517A) was connected to the probe and the current was measured in response to the applied voltage. The sample was compressed in the circular disk form with a diameter of 1.30 cm. The electrical conductivity of the samples was calculated using equation

$$\sigma = I/KVt$$

Where I is the measured current (A), V is the applied voltage (V), t is the sample thickness (cm) and K is the geometric correction factor which is equal to the ratio w/l , where w and l are the probe width and length, respectively (2.15×10^{-3}).

3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine Xerogels

Polybenzoxazine precursor was synthesized by dissolving CTAB (20 %wt) in N,N, -dimethylformamide (DMF) (47.56 g) and stirring continuously until CTAB was dissolved. Phenol (4.7 g) was then added into the mixture followed by adding formaldehyde solution (8.1 g). At the same time MDA solution was prepared

by adding MDA (4.72 g) into DMF (5 g) and stirring until MDA dissolved. The mixture that previously prepared was kept under 10°C by using an ice bath. MDA solution was slowly dropped into the mixture followed by continuous stirring for 20 minute at room temperature. The molar ration of phenol: formaldehyde: MDA was 2: 4: 1. And the concentration of polybenzoxazine sol-gel was kept at 25 % wt. The synthetic reaction is shown in Figure 3.1. After that the precursor was transferred into vial with seal and put into oil bath at 80°C for 24 hr, benzoxazine xerogels was taken out and cut into small pieces, then removed excess CTAB out via soxhlet method for 24 hr. Removed ethanol from benzoxazine xerogels by drying in the oven at 80°C overnight. The benzoxazine was placed in an oven by using the fully curing step at 110, 140, 150, 160, 170 $^{\circ}\text{C}$ and kept for 1 hr at each temperature and finally increased temperature from 170 to 180 $^{\circ}\text{C}$ for 40 minutes in order to polymerize benzoxazine xerogel which shown in Figure 3.2. After that DSC, TGA, and FT-IR were used to characterize polybenzoxazine xerogel.

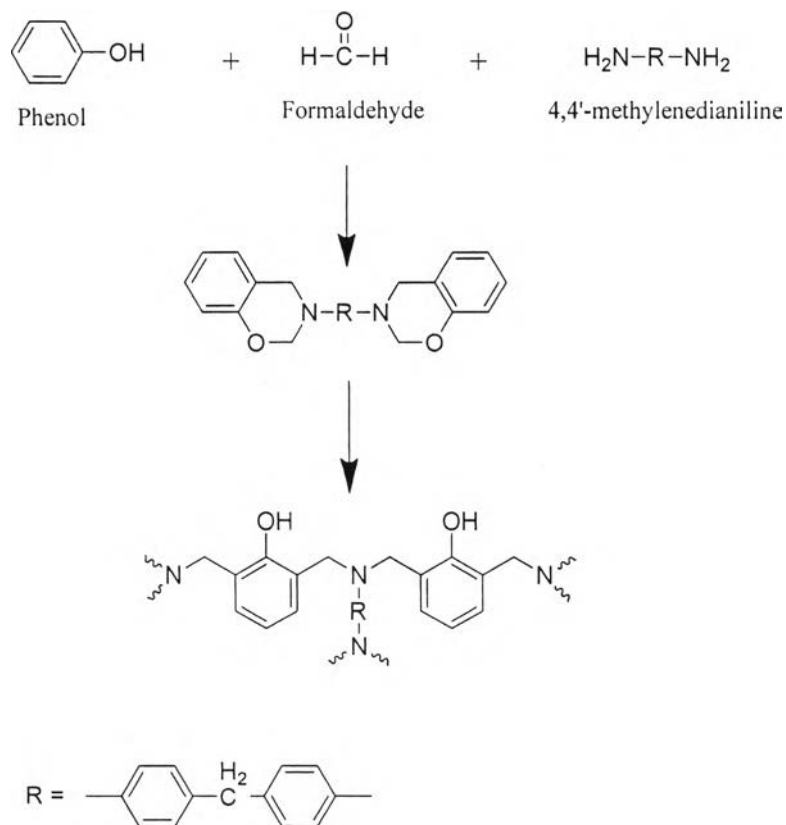


Figure 3.1 Preparation of polybenzoxazine precursor.

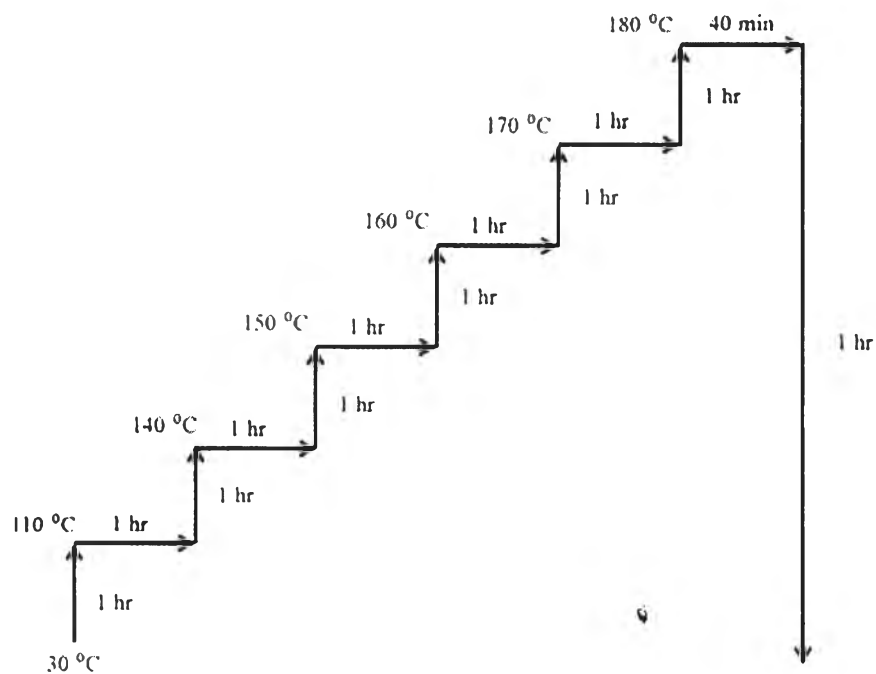


Figure 3.2 Curing steps of polybenzoxazine.

3.3.2 Preparation of Carbon Xerogels

Pyrolysis temperatures of polybenzoxazines were varied at 800, 900, and 1000 °C under a condition of nitrogen flow rate at 550 cm³/ min. The heating profile at each condition was shown on Table 3.1.

Table 3.1 The pyrolysis temperature of carbon xerogels

| 800 °C | | 900 °C | | 1000 °C | |
|-------------|------|-------------|------|-------------|------|
| Temperature | Time | Temperature | Time | Temperature | Time |
| 25-200 | 2 hr | 25-200 | 2 hr | 25-200 | 2 hr |
| 200-300 | 2 hr | 200-300 | 2 hr | 200-300 | 2 hr |
| 300 | 1 hr | 300 | 1 hr | 300 | 1 hr |
| 300-400 | 3 hr | 300-400 | 3 hr | 300-400 | 3 hr |
| 400 | 2 hr | 400 | 2 hr | 400 | 2 hr |
| 400-600 | 2 hr | 400-600 | 2 hr | 400-600 | 2 hr |
| 600-800 | 2 hr | 600-800 | 2 hr | 600-800 | 2 hr |
| 800 | 1 hr | 800-900 | 2 hr | 800-1000 | 2 hr |
| - | - | 900 | 1 hr | 1000 | 3 hr |

After that surface activation was required to improve wettability and surface area of carbon xerogels. Activated carbon xerogels (ACX) were prepared by using the heating profile from room temperature to 900°C for 3 hr and hold at 900°C for 3 hr in CO₂ atmosphere with flow rate 500 cm³ per minute.

3.3.3 Characterization of Polybenzoxazine and Carbon Xerogels

The chemical structure of polybenzoxazine precursor and polybenzoxazine were characterized by Fourier Transform Infrared (FT-IR) spectroscopy. TG-DTA and DSC were used to investigate the thermal properties.

X-ray diffraction (XRD) technique was used to examine the crystallographic of carbon xerogels. X-ray photoelectron spectroscopy (XPS) was used to investigate the ratio of C-C sp² and sp³ bond of carbon xerogels. Moreover, Raman spectra used to indicate structure and quality of carbon xerogels. Composition changing of carbon xerogels before and after surface activation was investigated by Vario EL III elemental analyzer.

Scanning electron microscopy (SEM) was used to examine the surface morphology and microstructure of polybenzoxazine and carbon xerogels.

The electrical property of carbon xerogels with various pyrolysis temperatures were observed by an electrometer with two-point probe (Keithley model 6517A).