



CHAPTER III EXPERIMENTAL

3.1 Materials

Bisphenol-A (BPA) was purchased from Aldrich, Germany. Formaldehyde (analytical grade) was purchased from Merck, Germany. Para-formaldehyde (commercial grade) was purchased from BDH Laboratory Supplies. Triethylenetetramine (TETA) was purchased from Fluka, Switzerland. Aniline (commercial grade) was purchased from Panreac Quimica SA Company. Sylgard 184 Silicone Elastomer Kit (PDMS) was purchased from Dow coming. Graphite (commercial grade) was purchased from Merck. Xylene (commercial grade) was purchased from Carlo Erba Reagenti. 1,4-Dioxane (analytical grade), acetone (commercial grade), tetrahydrofuran (analytical grade) and methanol (analytical grade) were purchased from Lab-scan, Thailand.

3.2 Measurements

The FT-IR spectrum of benzoxazine precursor was obtained using a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. ^1H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument, using deuterated dimethyl sulfoxide as solvent. DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from 30° to 300°C at a heating rate of 10°C/min under a N_2 atmosphere with a flow rate of 10 ml/min. TG-DTA curve was collected on a Mettler Toledo TGA/SDTA 851e instrument. The sample was loaded on the platinum pan and heated from 30° to 900°C at a heating rate of 20°C/min under N_2 flow of 50 mL/min. Scanning electron microscope, JEOL/JSM model 5200, was used to observe the surface morphology of polybenzoxazine-based aerogel and carbon aerogel. The specimens were coated with gold under vacuum before observation. Transmission electron microscope, JEOL model JEM-2100, was used to observe the porous structure of carbon aerogel. The

samples were prepared using the ultramicrotome. N₂ adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 250°C during 12 hr 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. Electrical resistivity of carbon aerogel-PDMS and graphite-PDMS composite films were measured using KEITHLEY 8009 electrometer to find the percolation threshold.

3.3 Methodology

3.3.1 Preparation of Carbon Aerogel Derived from Benzoxazine Precursor

Polybenzoxazine precursors were synthesized by dissolving bisphenol-A (4.52 g) in dioxane (20 ml) with stirring continuously, followed by adding formaldehyde (6.48 g) and triethylenetetramine, respectively. The mixture was stirred continuously while the reaction was cooled with an ice bath for 1 hr until the homogeneous viscous liquid was obtained. The mole ratio of bisphenol-A: formaldehyde:diamine was 1:4:1. The precursors were then heated in an oven at 80°C for 72 hr in a closed system to evaporate excess solvent, followed by fully curing organic aerogel by step cure in an oven at 140°, 160°, 180°C for 2 hr at each temperature and 200°C for 3 hr. After step-curing, carbon aerogels were prepared by pyrolysis of the organic aerogels in a quartz reactor. The pyrolysis took place in a furnace under nitrogen flow at 700 cm³/min using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min and held at 800°C for 60 min. Then the furnace was cooled down to room temperature under nitrogen atmosphere.

3.3.2 Synthesis of Carbon Aerogel from Polybenzoxazine Prepared from Monomer

The benzoxazine monomers were synthesized from bisphenol A, aniline, and paraformaldehyde at a 1:2:4 molar ratio were mixed together and heated at 110°C for 1 hr until the mixture became transparent pale yellow color.

Benzoxazine solutions were prepared from 40 wt% benzoxazine monomer in xylene solvent. The mixtures were transferred into vials and sealed before placing in an oven set at 130°C for 96 hr for the pre-curing process. The aerogels were step-cured in an oven at 160°, 180°C for an hour at each temperature and 200°C for 2 hr, respectively. After step-curing, carbon aerogels were prepared by pyrolysis of the organic aerogels in a quartz reactor. The pyrolysis took place in a furnace under nitrogen flow at 500 cm³/min using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min and held at 800°C for 60 min [18].

3.3.3 Characteristics of Polybenzoxazine and Carbon Aerogel Derived from Polybenzoxazine

Structural characteristics of polybenzoxazine-based aerogel were investigated using FTIR and ¹H-NMR. Thermal properties were measured using DSC and TG/DTA. Morphology was observed by SEM. Porous structure of polybenzoxazine-based aerogel was characterized by TEM. Furthermore, surface area and pore distribution were measured using SAA.

3.3.4 Preparation of Polydimethylsiloxane Composite Conductive Films

Polydimethylsiloxane composite conductive films were prepared by mixing three types of conductive fillers; carbon aerogel derived from Ba-TETA (abbreviated as CA_{TETA}), carbon aerogel derived from BA-a (abbreviated as CA_{BA}) and graphite with polydimethylsiloxane at various concentrations. The mixtures were then stirred continuously for 10 min until the conductive fillers are well dispersed. The mixtures were then cast on the glass plates with the film thickness of 1 mm. Finally, the films were kept at 80°C for 24 hr, yielding PDMS conductive composite films.

3.3.5 Electrical Response Measurements of Polydimethylsiloxane Composite Conductive Film

Electrical resistivities of CA_{TETA}/PDMS, CA_{BA}/PDMS and graphite/PDMS composite films were measured using KEITHLEY 8009 electrometer to determine the percolation threshold. Adsorption measurements of composite films in organic vapors were carried out as follows: firstly, the samples

were kept in a vacuum cavity before flowing saturated organic vapor, produced directly from the organic solvent located at the bottom of a seal gas vessel, at a temperature of 35°C. The composite films weighing approximately 10 mg were used to evaluate the adsorption behavior of the sample when exposed to several organic vapors. The adsorption quantity (Q_t) of the sample was determined from $Q_t = \Delta m/m_0$, where Δm is the mass increment of the sample in vapors, and m_0 is the original mass.