

CHAPTER III EXPERIMENTAL

3.1 Materials and Chemicals

1. Bisphenol-A (Aldrich), (100% purity), 500 g
2. Formaldehyde (Merck), (37%wt. in water), 1 L
3. 4,4'-Methylenedianiline (MDA) (Aldrich), 1 Kg
4. Polydiallyldimethylammonium chloride (PolyDADMAC) (Aldrich), (20%wt. in water), 1 L
5. polystyrenesulfonate (PSS, sodium salt, MW 70,000), Sigma Aldrich, 250 g
6. Humic acid (Aldrich), 100 g
7. Sodium hydroxide (Univar), 1 kg
8. Sodium chloride (Carlo Erba), 1 kg
9. Copper (II) acetate (Fisher Scitific), 100g
10. *N,N*-Dimethylformamide (DMF) (Lab-Scan), 4 L
11. Acetone (Lab-Scan), 4 L

3.2 Measurements

3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

A Fourier Transform Infrared Spectroscopy (FT-IR), Nicolet Nexus 670, was used to identify structural characteristics of polybenzoxazine, polybenzoxazine coated PDADMAC, PSS, humic acid and heavy metal in adsorption mode. They were mixed with potassium bromide (KBr) to prepare powder samples.

3.2.2 Ultraviolet-visible spectroscopy (UV-VIS)

The absorbance of polybenzoxazine coated PDADMAC, PSS, humic acid was investigated by using Ultraviolet-visible spectroscopy.

3.2.2 Scanning Electron Microscopy (SEM-EDX)

The morphology of polybenzoxazine xerogel was investigated by using scanning electron microscope, Hitachi S-4800, with an accelerating voltage of 2 kV. Samples were coated with Platinum under vacuum before observation. Samples were coated with platinum under vacuum before observation. In addition, the amount of metal ion on the surface can be determined by EDX mode.

3.2.3 Surface Area Analyzer (SAA)

The surface area, average pore size, total pore volume and micropore volume of polybenzoxazine xerogel was investigated by using Surface area Analyzer; Quantachrome, with outgas time 12 hours.

3.2.4 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter (DSC), METTLER, was used to study the thermal behavior of partially-cured and fully-cured polybenzoxazine. The samples were heated from 30 °C to 200 °C at a heating rate of 10 °C/min under N₂ atmosphere with a flow rate of 20 ml/min.

3.2.5 Thermogravimetric/Differential Thermal Analyzer (TG-DTA)

The thermal property of polybenzoxazine xerogel was investigated by using Thermo gravimetric Analyzer; Perkin Elmer, with heating rate 20°C/min. Platinum pan was used as a reference pan and heated from 30° to 300°C.

3.3 Experimental

3.3.1 Preparation of Benzoxazine Precursor

Bisphenol-A and MDA were dissolved into DMF in glass bottles. Formaldehyde was then added into the bisphenol-A solution and stirred continuously for one hour until homogeneous yellow viscous liquid was obtained. The temperature is kept under 10°C using an ice bath. After that MDA solution was added into the mixture. The ratio of bisphenol-A, formaldehyde and MDA is 1:4:1. The

benzoxazine precursor was identified structural characteristic by using FTIR measurement.

3.3.2 Preparation of Polybenzoxazine Xerogel

The benzoxazine precursor was transferred into vials and sealed then heated in the oil bath at 80 °C for 48 h in a closed system, followed by evaporating the solvent at ambient condition for one day.

3.3.3 Preparation of Polymer Solutions (PDADMAC, PSS) and Humic Acid

The solutions were prepared by dissolving 1 mM PDADMAC, 1 mM PSS and 0.1 % Humic acid in distilled water, followed by adding 1.0 M NaCl to PDADMAC and PSS, 0.3 M NaCl to PDADMAC and Humic acid and adjust pH to 9-10 by adding of 0.1 M NaOH solution.

3.3.4 Preparation of Glass Slide Coated with Polymer Solutions (PDADMAC, PSS) and Humic Acid (Layer-by-Layer Method)

A glass slide was rinsed by distilled water before use and then achieved with a primary coating formed by 4 layers of PDADMAC with 1.0 M NaCl and PSS followed by a secondary coating of PDAD-Humic with 0.3 M NaCl respectively for 2, 4, 6, and 8 layers. Rinsed a glass slide by distilled water for each layer and then a glass slide was dried for 4 days at room temperature in the box. The coating of polymer solutions was confirmed by using reflectance UV-VIS Spectroscopy.

3.3.5 Surface Modification of Polybenzoxazine Xerogel Coated with Polymer Solutions (PDADMAC, PSS) and Humic Acid (Layer-by-Layer Method)

After the polybenzoxazine xerogel was evaporated over night, it was cut with the thickness of 3 mm. A polybenzoxazine precursor was passed through by distilled water before use. It was coated with a primary coating formed by 4 layers of PDADMAC with 1.0 M NaCl and PSS, followed by a secondary coating of PDADMAC-Humic with 0.3 M NaCl for 2, 4, 6, and 8 layers, respectively. After

finishing coating each layer, the precursor was rinsed with distilled water. The coating of polymer solutions was confirmed by using UV-VIS Spectroscopy.

3.3.6 Preparation of Layer-by-Layered Polybenzoxazine Xerogel for Copper Removal

The obtained polybenzoxazine xerogel was then fully cured by step curing in an oven. The synthetic reaction is shown in Figure 3.1

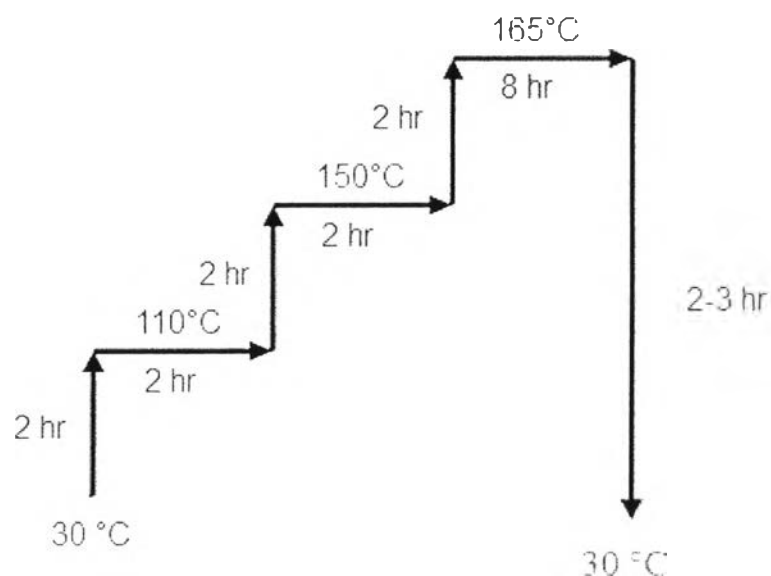


Figure 3.1 Schematic of a step of curing.

3.3.7 Copper Removal

To study the interaction between copper and humic acid, the injection time was varied from 1 to 120 min. Copper (II) acetate solution with 250, 500, 1000 ppm concentration was slowly injected through the surface of polybenzoxazine xerogel coated with layer-by-layer method.