CHAPTER III
EXPERIMENTAL

3.1 Materials

All chemicals were used without further purification. The benzoxazines was synthesized using various types of amine; aniline (99%) was purchased from Panreac Company, 4,4'-methylenedianiline (≥97%), paraformaldehyde powder (95%) and tetraethylenepentamine (95%) were purchased from Sigma-Aldrich Co., Ltd and Phenol detached crystals (99.99%) was obtained from Fisher Chemical company. Silver nitrate was used to enhanse thermal properties of benzoxazines and purchased from VRBIOSCIENCE Co., Ltd.

3.2 Equipments

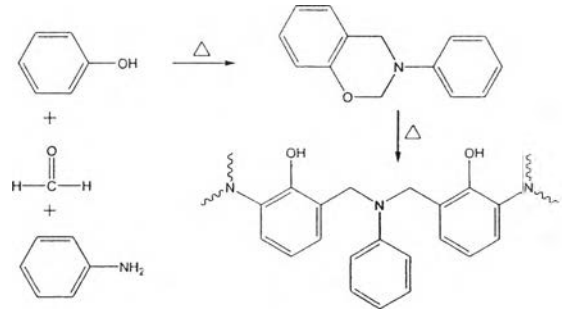
The functional groups related to structure of materials were investigated by using FTIR technique. The FT-IR spectra were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 400-4000 cm^{-1} with 64 scans at a resolution of 2 cm^{-1}. KBr pellet technique was applied in the preparation of powder samples. DSC analyzer was carried out using a Perkin-Elmer DSC 7 instrument. The sample was heated from 50 to 300 °C with heating rate 10 °C per minute under N_2 gas 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 800 °C under nitrogen gas 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 was obtained using an XRD (Bruker AXS D8 ADVANCE) spectrometer with Cu Kα irradiation (λ = 0.15406 nm) at 40 kV and 30mA to examine the graphitization of the

partially ordered carbon after carbonization. Surface area analyzer (SAA) was used to determined surface area, pore volume and pore size distribution of activated carbon. The results were obtained by Quantachrome/Autosorb-1 based on the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) using nitrogen adsorption isothermal at 77 K. The sample wasloaded around 0.2 g and removed gas at 250 °C. The electrical conductivity values of the partially ordered carbons were obtained by measuring the resistances and calculate the electrical conductivity. The geometric correction factor was determined by calibrating the four-point probe with semi-conducting silicon sheets of known resistivity values. Applied dc currents were small to be in the linear Ohmic regime. The electrical conductivity of the partially ordered carbon was observed at room temperature by an electrometer with two-point probe (Keithley model 6517A)

3.3 Methodology

3.3.1 Synthesis of Aniline-based Polybenzoxazine (PBZ-A)

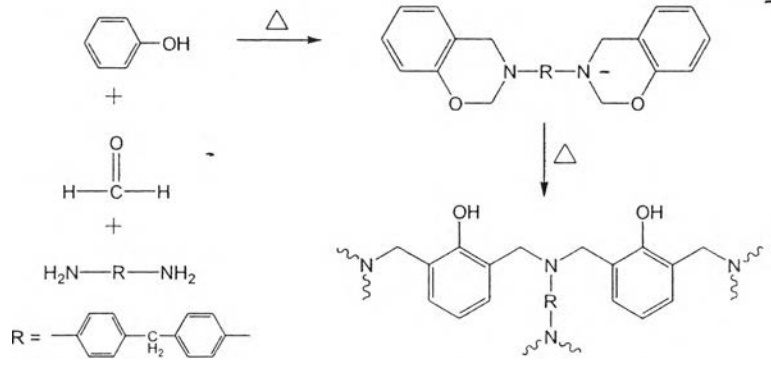
The solventless method invented by Ishida (1996) was used to synthesize benzoxazine prepolymer with a mole ratio of Phenol: Aniline: Paraformaldehyde is 1: 1: 2. The mixtures of phenol, paraformaldehyde and aniline were heated at 100 °C until they change to be transparent yellow viscous. From this step, aniline-based benzoxazine precursor (BZ-A) was obtained. Before curing step, the benzoxazine precurcers were grinded and then cured at 245 °C for 1 h in ambient air. Finally, aniline-based polybenzoxazine will be obtained.



Scheme 3.1 Synthesis of aniline-based polybenzoxazine.

3.3.2 Synthesis of Methylenedianiline-based Polybenzoxazine (PBZ-MDA)

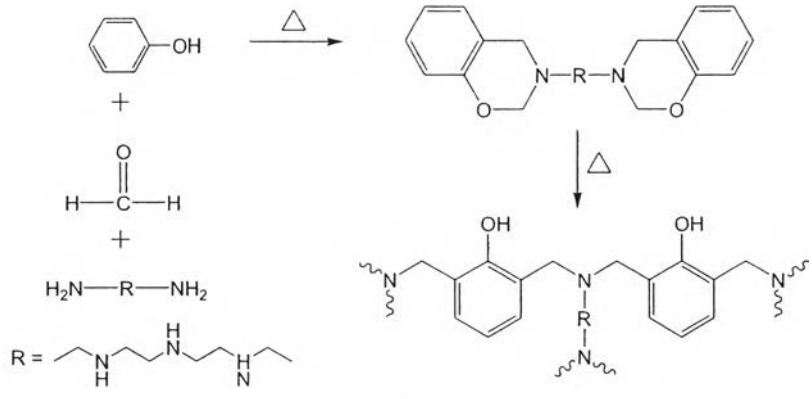
The mixtures of phenol, paraformaldehyde and methylenediamline with ratio 2: 4: 1 were heated at 100 °C until they change to be transparent yellow viscous. From this step, methylenedianiline-based benzoxazine precursor (BZ-MDA) was obtained. Before curing step, the benzoxazine precurcers were grinded and then cured at 235 °C for 1 h in ambient air. Finally, methylenedianiline-based polybenzoxazine will be obtained.



Scheme 3.2 Synthesis of methylenedianiline-based polybenzoxazine.

3.3.3 Synthesis of Tetraethylenepentamine-based Polybenzoxazine (PBZ-TEPA)

The mixtures of phenol, paraformaldehyde and tetraethylene-pentamine with ratio 2: 4: 1 were heated at 100 °C until they change to be transparent yellow viscous. From this step, tetraethylenepentamine-based benzoxazine precursor (BZ-TEPA) was obtained. Before curing step, the benzoxazine precurcers were grinded and then cured at 260 °C for 1 h in ambient air. Finally, tetraethylene pentamine-based polybenzoxazine will be obtained.



Scheme 3.3 Synthesis of tetraethylenepentamine-based polybenzoxazine.

3.3.4 Synthesis of Methylenedianiline-based Polybenzoxazine with Silver Nitrate (PBZ-MDA- $AgNO_3$)

The methylenedianiline-based benzoxazine precursor that was obtained from previous step and silver nitrate were mixed together with weight ratio 10: 1. The mixtures were heated at 100 °C until they change to be homogeneous brown viscous. Before curing step, the benzoxazine precurcers were grinded and then cured at 217 °C for 1 h in ambient air. Finally, methylenedianiline-based polybenzoxazine with silver nitrate will be obtained.

3.3.5 Preparation of Partially Ordered Carbon by Pysolysis (NC)

Fully cured polybenzoxazines base on various types of amine were pyrolyzed at 500, 800 and 1200 °C with heating rate 2 °C per minute and under N_2 with flow rate 500 cm^3 per minute. Partially ordered carbons have been obtained after the temperature goes to room temperature. Partially ordered carbons base on aniline, methylenedianiline and tetraethylenepentamine were abbreviated to NC-A, NC-MDA and NC-TEPA respectively. For activated carbons base on methylenedianiline with silver nitrate were abbreviated to NC-MDA-$AgNO_3$.

3.3.6 Preparation of Activated Carbon

Obtained partially ordered carbons by pyrolysis were activated at 900 °C for 3 h under CO_2 with flow rate 500 cm^3 per minute. Partially ordered carbons have been obtained after the temperature goes to room temperature. Activated carbons base on methylenedianiline was abbreviated to AC-MDA.

3.3.7 Characterization of Polybenzoxazine and Nanocabon

The effects of the pyrolysis temperatures on the microstructure of the obtained partially ordered carbon have been investigated. The changing in chemical structures of polybenzoxazine was examined by FTIR. Moreover, TGA was used to investigate the thermal properties. The physical properties of the products were also investigated by SAA. In addition, XRD was used to demonstrate the characteristics d spacing of the resulting partially ordered carbon. The electrical property of partially ordered carbon was observed at room temperature by an electrometer with two-point probe (Keithley model 6517A)