CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Bisphenol-A (BA, 97%, Sigma Aldrich Chemicals Co. Inc., USA)
2. 4,4'-Methylenedianiline (97%, Sigma Aldrich Chemicals Co. Inc., USA)
3. Formaldehyde solution (37%, Merck Limited., Gemany)
4. *N,N*-Dimethlyformamide (DMF, Lab-scan Asia Co., Ltd., Thailand.)
5. Acetone (Commercial Grade, Lab-scan Asia Co., Ltd., Thailand.)
6. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Sigma Aldrich Chemicals Co. Inc., USA)

3.2 Equipment

1. Nicolet/Nexus 670 Fourier Transform Infrared spectrometer (FTIR)
2. JEOL/JSM 5200 Scanning Electron Microscope (SEM)
3. Thermogravimetric Analyzer- Fourier Transform Infrared spectrometer (TGA-FTIR)
4. Quantachrome/Autosorb^{-1}Surface Area Analyzer (SAA)
5. Universal testing machine (Lloyd, model SMT2-500N)
6. Glassware
7. Oven
8. Water bath
9. Furnace

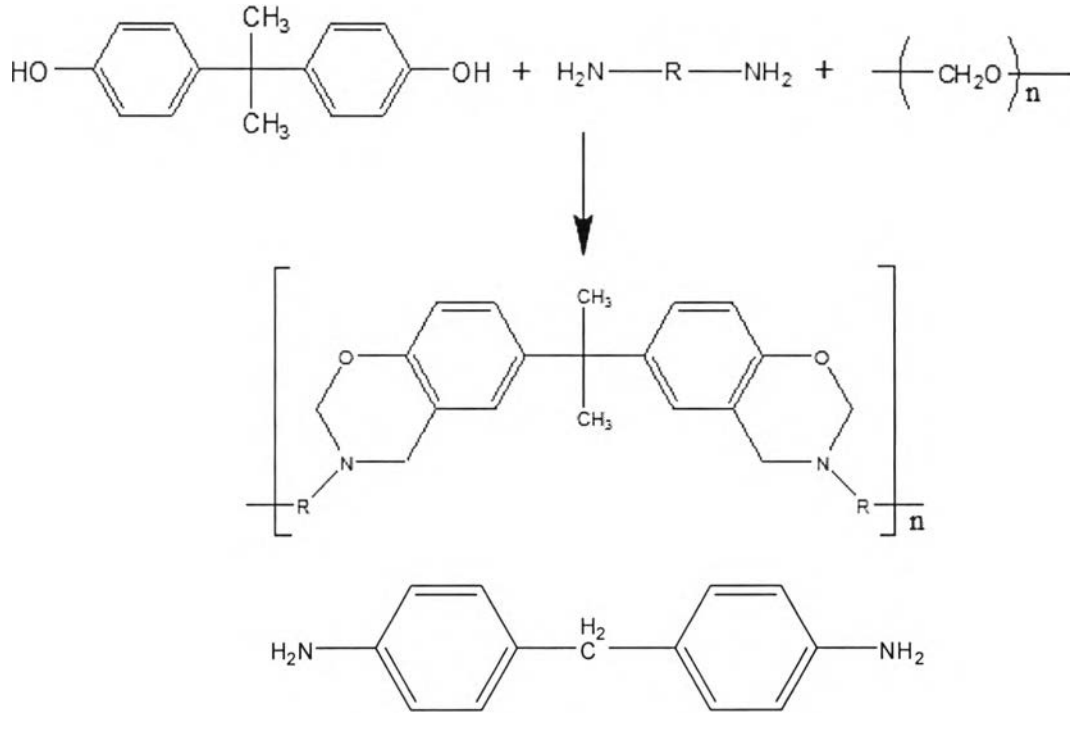
Software:

1. Omnic
2. Sigma Plot 11.0

3.3 Methodology

3.3.1 Synthesis of polybenzoxazine-based carbon xerogels (PBZ-based organic xerogels)

The PBZ was synthesized by sol-gel method and ambient drying process. The molar ratio of reactant sol was Bisphnol-A, TETA or MDA and formaldehyde 1:1:4, respectively. The solid content of PBZ was fixed at 25% w/w. Bisphenol-A was dissolved in DMF. Afterwards, formaldehyde and non-ionic surfactant (Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)) was then added and continuously stirred for 20 minutes. Finally, TETA or MDA was slowly dropped into the mixture and continuously stirred for 1 h while the reaction was cooled with an ice bath until a homogeneous yellow liquid was obtained. After that, the mixture was transferred into a vial and seal at room temperature for one night then placed it in an oil bath at 80°C for 2 days.



4,4-Diaminodiphenylmethane (MDA)

Figure 3.1 Structure of the Benzoxazine precursor.

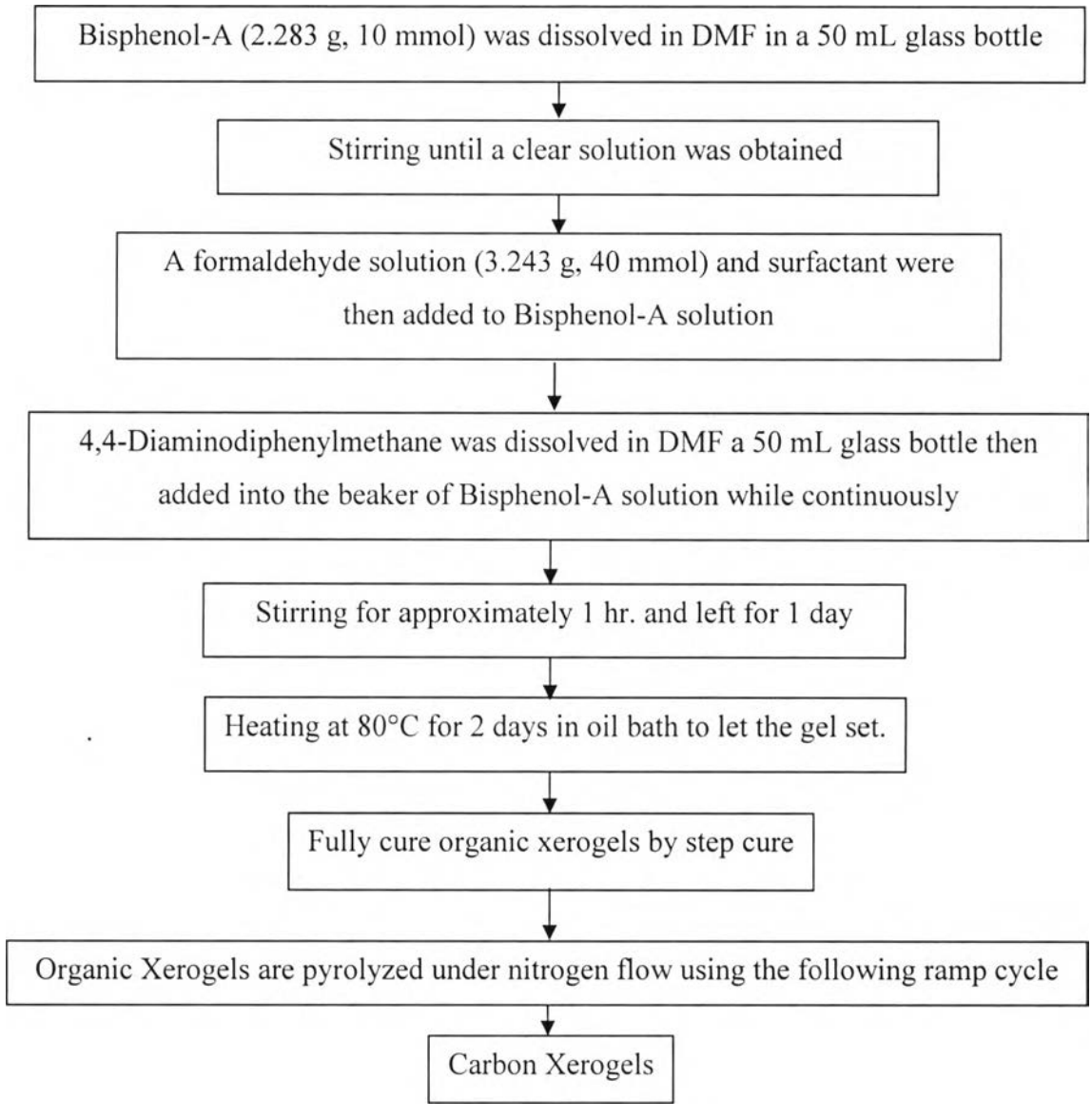


Figure 3.2 The synthesis of carbon xerogels from polybenzoxazine precursors.

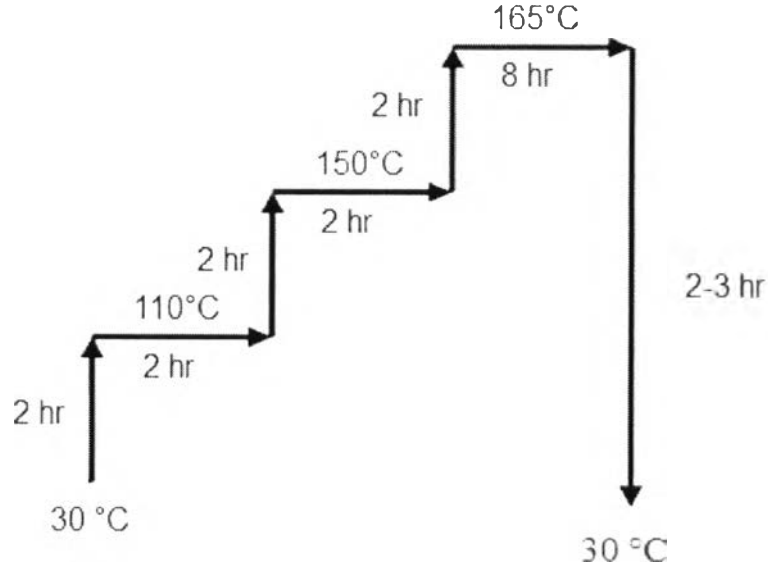


Figure 3.3 Schematic of a step of curing.

3.3.2 Identification of microstructure and morphology of polybenzoxazine-based organic and carbon xerogel

The chemical structure of benzoxazine precursor was identified by using Fourier transform infrared (FT-IR) spectroscopy, which recorded on a Nicolet Nexus 670 FT-IR spectrometer by using KBr pellet technique. Differential Scanning Calorimeter (DSC), METTLER, was used to study the thermal behaviors of partially-cured and fully-cured polybenzoxazine. The morphology and microstructure of carbon xerogels were observed by field emission scanning electron microscope (FE-SEM, Hitachi/S-4800 model) and transmission electron microscope (TEM, JEOL 2010F). Quantachrome-Autosorp1-MP was used to determine the pore structure of the samples. Approximately 0.1 g of carbon xerogels was degassed at 250 °C for 18 h to remove all the adsorbed species. The specific surface area (S_{BET}) was calculated by BET algorithm (Brunauer-Emmett-Teller). Micropore volume (V_{mic}) wws analyzed by the t-plot method. Micropore size distribution was analyzed by MP method (Standard micropore size distribution). Mesopore volume (V_{mes}) and mesopore size distributions were analyzed by BJH (Barrett-Johner-Halendar) algorithm. The skeletal density (ρ_s) of samples was measured by gas pycnometer

(Ultrapycnometer, Quantachrome Intrument). The mass (m) and volume (V) of samples were measured and the bulk density (ρ) was calculated from the following formula.

$$\rho = m / V$$

The micropore volume (V_{mic}) was analyzed by the t-plot method at the relative pressure of less than 0.1[3]. Mesopore volume (V_{mes}) and mesopore size distribution were analyzed by the BJH (Barrett-Johner-Halendar) method[4,5]. Macropore volume (V_{mac}) and total pore volume were calculated according to the Wu et al.'s method[6], Briefly, total pore volume was calculated from the following equation: $V_{total} = (1/\rho) - (1/\rho_s)$ where ρ is the bulk density and ρ_s is the skeletal density. Macropore volume was determined by subtraction of total pore volume from micro- and meso- pore volume as shown in the following equation[6]: $V_{mac} = V_{total} - V_{meso} - V_{micro}$.