

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Sample Preparation

The material used in this research is bifunctional benzoxazine resin. This benzoxazine resin is based on bisphenol-A, aniline, and formaldehyde. Commercial grade bisphenol-A was supplied by Bayer Thai Co., Ltd. Para-formaldehyde (95%) was purchased from BDH Laboratory Supplies. Aniline (99%) was purchased from Panreac Quimica SA Company, and the solvent, xylene (98%), was obtained from Carlo Erba Reagenti. Azodicarbonamide (AZD) (Supercell-VR207), used as a foaming agent, was provided by A.F. Supercell Co., Ltd. Untreated chopped glass fiber (Jushi group Ltd.) with average length of 3 mm was selected as reinforcement for foam composite fabrication.

#### 3.1.1 Organic and Carbon Aerogel Preparation

A benzoxazine monomer was synthesized via the solventless process proposed by Ishida *et al.* (1996). Bisphenol A, aniline, and paraformaldehyde, at a 1:2:4 molar ratio, were mixed together and heated at 110 °C. Benzoxazine solutions were prepared from the benzoxazine monomer using xylene as a solvent. The monomer concentrations were kept at 20 and 40 wt%. After that, the mixtures were heated 130 °C for 96 h in an oven. Then, the aerogels were dried and step-cured. The specimens were finally left to cool to room temperature and were then ready for further characterization. After step-curing, the carbon aerogels were prepared by the pyrolysis of the organic aerogels in a quartz reactor.

#### 3.1.2 Organic and Carbon Foam Preparation

The same procedure as the aerogel preparation is applied, benzoxazine monomer was synthesized via the solventless process. The solidified benzoxazine monomer was ground into a fine powder. After that, azodicarbonamide (AZD) was added into the monomer powder with different weight ratios. In order to obtain foam composite, the benzoxazine monomer with specified AZD content was combined

with different weight ratios of glass fiber. The obtained mixture was melt-mixed and then transferred to an aluminum mold and heated from 30 to 210 °C using a heating rate of 1 °C/min under atmospheric conditions. The attained product was a cured polybenzoxazine foam and foam composite, which was ready for further characterizations. For carbon foam preparation, the polybenzoxazine foam was carbonized in a quartz reactor. The carbonization took place in a tube furnace under inert atmosphere.

### 3.2 Characterization of Polybenzoxazine Aerogel and Polybenzoxazine Foam

#### 3.2.1 Physical Analysis

The densities of the aerogel and foam samples were determined by weighing the geometrically shaped samples and dividing the weight by the measured volume. The void volume fraction of the samples was estimated using ASTM D-2734. The void volume fraction was calculated, using the equation below.

$$\text{Void volume fraction} = \frac{100 \times (q_{\text{theoretical}} - q_{\text{measured}})}{q_{\text{theoretical}}}$$

where  $q_{\text{theoretical}}$  is the theoretical density of polybenzoxazine and  $q_{\text{measured}}$  is the measured density of the resulting porous materials.

The microstructures of the aerogel and foam samples were observed by scanning electron microscopy (SEM) using JEOL-JSM 5800LV and Olympus SZ-4045-TR optical microscope. Moreover, in order to investigate highly magnified microstructures of the obtained aerogels, H-7650 Hitachi High-Technologies transmission electron microscope (TEM) system was employed.

The porous structure of the carbon aerogels was measured by the nitrogen adsorption method in order to acquire the surface area, pore volume, pore size, and pore size distribution of the samples. Nitrogen adsorption–desorption isotherms were measured using a Quantachrome-Autosorb-1.

### 3.2.2 Structural Analysis

The IR spectra of the samples in this study were recorded by a Thermo Nicolet Nexus 670 FT-IR analyzer. In order to examine the graphitization of the sample after carbonization, XRD (Bruker AXS D8 ADVANCE) spectrometer was utilized to obtain a diffraction pattern.

### 3.2.3 Thermal Analysis

Thermal behaviors of benzoxazine monomer, polybenzoxazine aerogel, foaming agent, and benzoxazine monomer/foaming agent mixture were investigated by using a PerkinElmer Differential Scanning Calorimeter, DSC 7, analyzer to get useful synthesis parameters for the aerogel and foam processing. PerkinElmer's TG/DTA thermo gravimetric analyzer, model SII Diamond, was used to examine the decomposition temperature and char yield of the polybenzoxazine in this study.

### 3.2.4 Mechanical and Thermomechanical Analysis

Using ASTM D 1621 as the standard, an INSTRON universal testing instrument (Model 4502), with a 15 kN static load cell, was used to determine the uniaxial compression properties of the samples. DMA (NETZSCH DMA 242) was used to characterize the thermomechanical properties of the samples, which the thermograms were obtained with a heating rate of 5 °C/min.

### 3.2.5 Electrical Analysis

The electrical conductivity of resulting carbon foam was measured by the standard four-point probe method with a current of 10 mA.

### 3.2.6 Thermal Decomposition Investigation

The chemical structures of the volatile decomposition products generated during the thermogravimetric analysis were performed using a TGA Q50 with coupled to a Thermo Nicolet Nexus 670 FT-IR analyzer. Furthermore, the volatile decomposition products from TGA/DTG were also identified by GC-TOF-MS analysis (GC7890A, Agilent Technologies, Palo Alto, CA, USA, and PEGASUS

4D TOF-MS, LECO Instrumente GmbH, Mönchengladbach, Germany) using Rtx-5 (RESTEK) 10m x 0.18mm x 0.20 $\mu$ m and Rtx-17 (RESTEK) 1.1m x 0.10mm x 0.10 $\mu$ m columns.

### 3.2.7 Kinetic Analysis

For kinetic analysis of the samples, the Kissinger model was applied to the overlapping peaks within the DTG thermogram and to separate the peaks of the DTG thermogram, nonlinear curve fitting was achieved by using Peak Fit program.

The relevant equation is:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_a} + \ln[n(1 - \alpha_p)^{n-1}] - \frac{E_a}{RT_p}$$

where  $n$  is the apparent reaction order,  $T_p$  is the absolute temperature at which the maximum weight-loss rate occurs,  $\alpha_p$  is the fraction of decomposition at maximum weight-loss rate, and  $\beta$  is the heating rate in the experiment.