

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Poly(propylene glycol) tolyene 2,4-diisocysnate terminated, average M.W. 2300 (Aldrich)
- Paraformaldehyde, 98.7% (Merck.)
- Bisphenol A , 99% (Aldrich)
- Aniline, 99% (Panreac.)
- 4,4'-Diaminodiphenylmethane, $\geq 97\%$ (Aldrich)
- Hexamethylenediamine, 98% (Aldrich)
- Sodium bicarbonate ACS reagent, 99.7-100.3% (Aldrich)
- Sodium sulfate ACS reagent; anhydrous, granular, $\geq 99.0\%$ (Aldrich)
- Barium acetate, 99% (Aldrich)
- Strontium acetate hydrate, 99.995% (Aldrich)
- Titanium tetra-n-butoxide, 97% (Aldrich)
- 3-aminopropyl trimethoxy silane, 97% (Aldrich)

3.1.2 Solvents

- Methanol, AR (Lab scan)
- Glacial acetic acid (Lab scan)
- Chloroform, AR (Lab scan)
- Dimethylformamide, AR (Lab scan)

3.2 Experimental Procedures

3.2.1 Synthesis of Aniline-Based Benzoxazine Monomer (BA-a)

The synthesis of aniline-based benzoxazine monomer was prepared via the reaction of bisphenol A, paraformaldehyde and aniline at the molar ratio of 1:4:2, respectively through solventless method as shown in Figure 3.1. The combination of raw materials was heated to 110°C for 30 min. The obtained viscous solution with high yellow was cool down and ground into powder. Then the final product was further purified in order to remove any unreacted starting materials. The powder was washed at least 3 times by using cool methanol and dried before used.

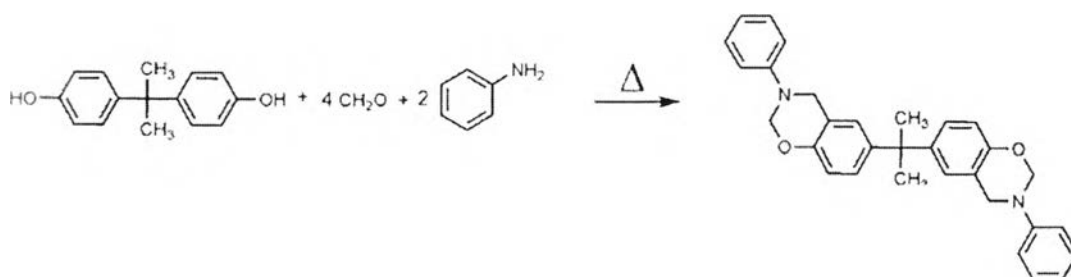


Figure 3.1 Synthesis of aniline-based benzoxazine monomer (BA-a) (Ghosh *et al.*, 2007).

3.2.2 Synthesis of Methylendianiline- (BA-mdm) and Hexamethylenediamine-Based (BA-hda) Benzoxazine Precursors

To Synthesize BA-mdm precursor through the solvent method, mdm (0.080 mol, 15.86 g), bisphenol-A (0.080 mol, 18.26 g) and paraformaldehyde (0.344 mol, 10.30 g) were added into 250 ml round-bottom flask with 200 mL of chloroform as the solvent. The reaction was carried out under reflux at 100°C for 6 h. The obtained mixture was filtered and sequentially washed with 0.5 N NaHCO₃ aqueous solution (400 mL). To eliminate water, the sample solution was dried with anhydrous sodium sulfate for one night. After evaporation, the white crystal benzoxazine precursors were solid at room temperature. The synthesized precursors were ground into a fine powder and taken for material characterizations. Preparation of BA-hda used the same approach, substituting hda in the place of mdm.

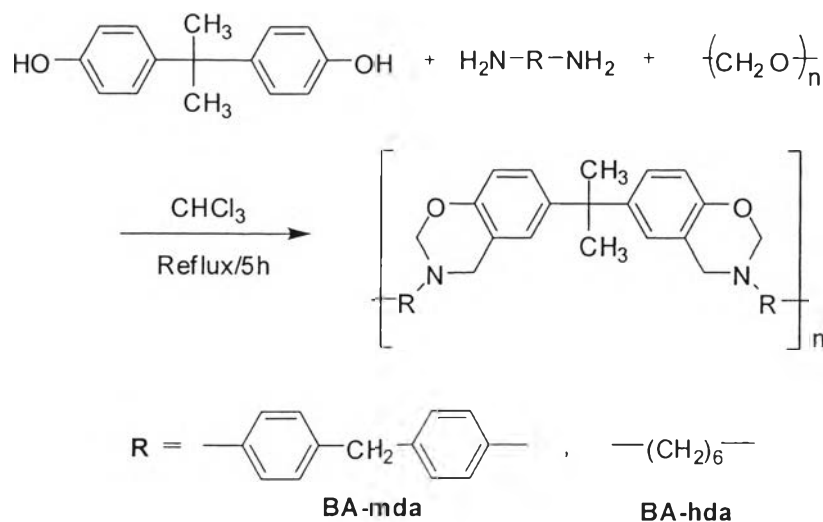


Figure 3.2 Chemical route for synthesis of methylenedianiline- (BA-mda) and hexamethylenediamine-based (BA-hda) benzoxazine precursors (Tsutomu T. et al. 2005)

3.2.3 Preparation of poly(BA-mda) and poly(BA-hda) specimens

The BA-mda precursors (~2 g) were dissolved in 3 g of dimethylformamide. Firstly, the mixture was heated to 100 °C and vigorously stirred until becoming a homogeneous solution. The solution was then poured into an aluminium mold. To avoid bubbles being trapped inside the specimen, the temperature was gradually increased up to 200°C. After the curing process, the fully cured specimen gave the transparent dark brown and was used for characterizations. The preparation of the BA-hda specimen was performed in the same way.

3.2.4 Preparation of poly(benzoxazine/urethane) specimens

The benzoxazine monomer (BA-a) was blended with the poly(propylene glycol) tolyene 2,4-diisocysnate terminated as urethane prepolymers (PU) to provide BA-a/PU mixtures. The fraction of urethane prepolymer was varying at 0, 10, 20, 30, and 50 vol. %. The mixture was then heated to about 120°C for 30 min. without solvent in aluminum pan and mixed until a homogeneous mixture was obtained. The molten resin mixture was poured into an aluminum mold and step cured in an air-circulated oven at 150 °C for 30 min., 170 °C for 30 min., and 200 °C for 2 hr. The vacuum was also applied some places in order to help reduce porous in

the specimens. Part of the mixture was taken for differential scanning analysis. The color of the cured samples changed from yellow to dark brown after the crosslinking process. The specimen was finally left to cool down to room temperature and was then ready for material characterizations.

3.2.5 Preparation of Barium Strontium Titanate by Sol-Gel Process

To prepare barium strontium titanate, $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (BST), 0.3 mole of barium acetate and 0.7 mole of strontium acetate were separately dissolved in glacial acetic acid, followed by the addition of methanol to each solution. Both of the completely soluble components were mixed together and then an equimolar amount of titanium (iv) n-butoxide was added into this mixture under vigorous stirring. After gel was formed, it was calcined by 2-step thermal decomposition to decompose the solvent and crystallize the BST powder. The calcination procedure is shown in Figure 3.3.

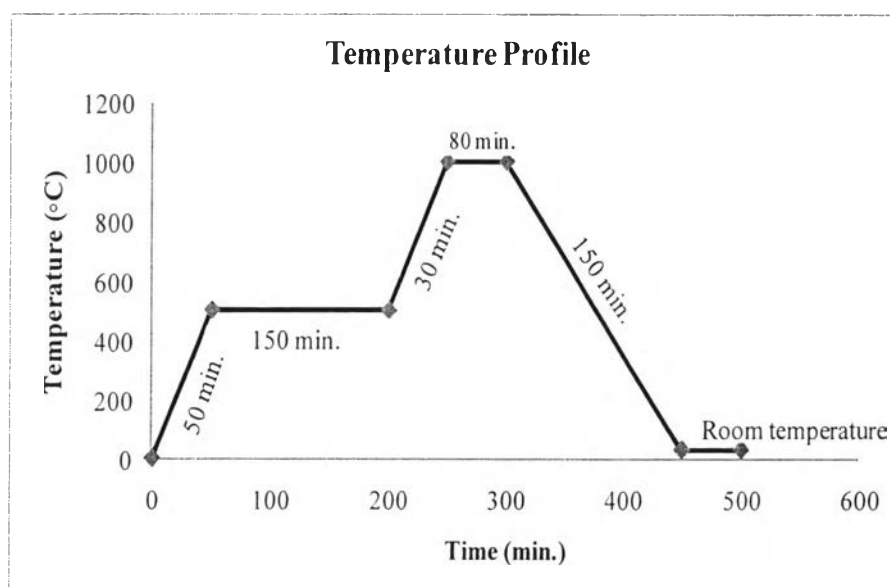


Figure 3.3 The temperature profile for two-step thermal decomposition of BST.

3.2.6 Composite Preparation

3.2.6.1 *Poly(benzoxazine/urethane) composites*

For composite fabrication, at 90/10 vol.% of BA-a/PU copolymer as a polymer matrix and BST ceramic ($\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$) were mixed together by varying BST content at 30, 40, 50, and 60 wt.% through melt mixing method to avoid phase separation. After that, the mixtures was prepared as composite specimens with the thickness of 1 mm. and 20 mm. in diameter with curing conditions which given in 3.3.4

3.2.6.2 *Poly(BA-mda) composites*

BA-mda was dissolved in dimethylformamide and vigorously stirred until obtaining homogeneous solution. Then BST powders at desirable amount (30, 40, 50, and 60 wt.% of BST) were added and followed by curing process as mention in 3.3.3.

3.2.7 Surface Modification of BST Powders

3.2.7.1 *Surface Modification by Silane Coupling Agent*

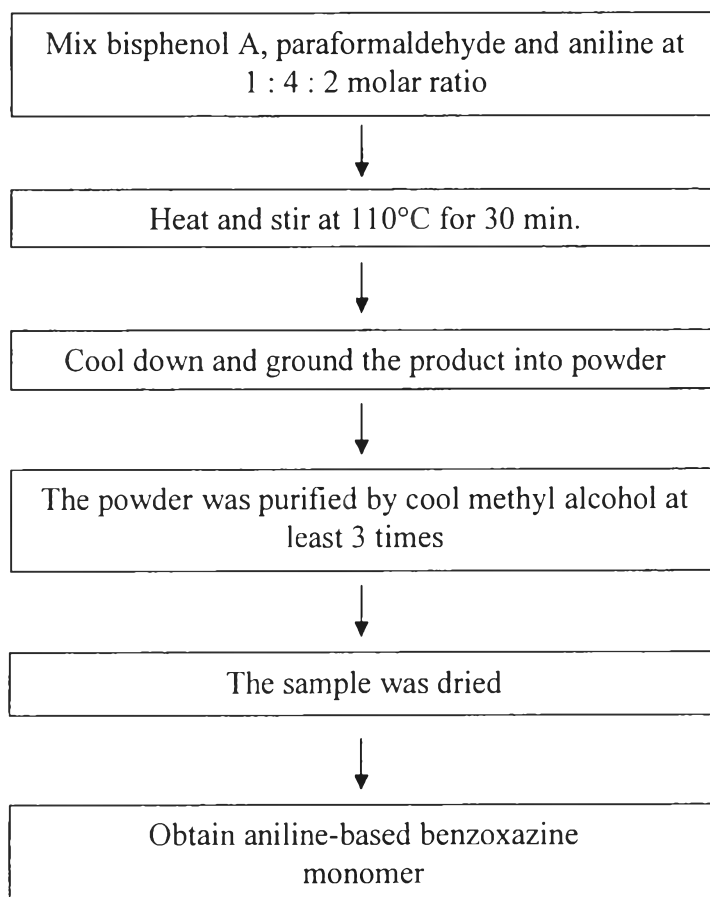
The 3-aminopropyl-trimethoxysilane (2 g) was dissolved in 5:95 ml of ethanol-water solution. Subsequently, the 40 g of BST powder was added into the mixture. This suspension was further dispersed in an ultrasonic chamber at room temperature for 10 min. and stirred at 70°C for 1 h. The colloidal solution was centrifuged and later washed off the residual by ethanol. After dried in a vacuum oven at 50°C, the silane treated BST particles were obtained.

3.2.7.2 *Surface Modification by BA-a/PU copolymer*

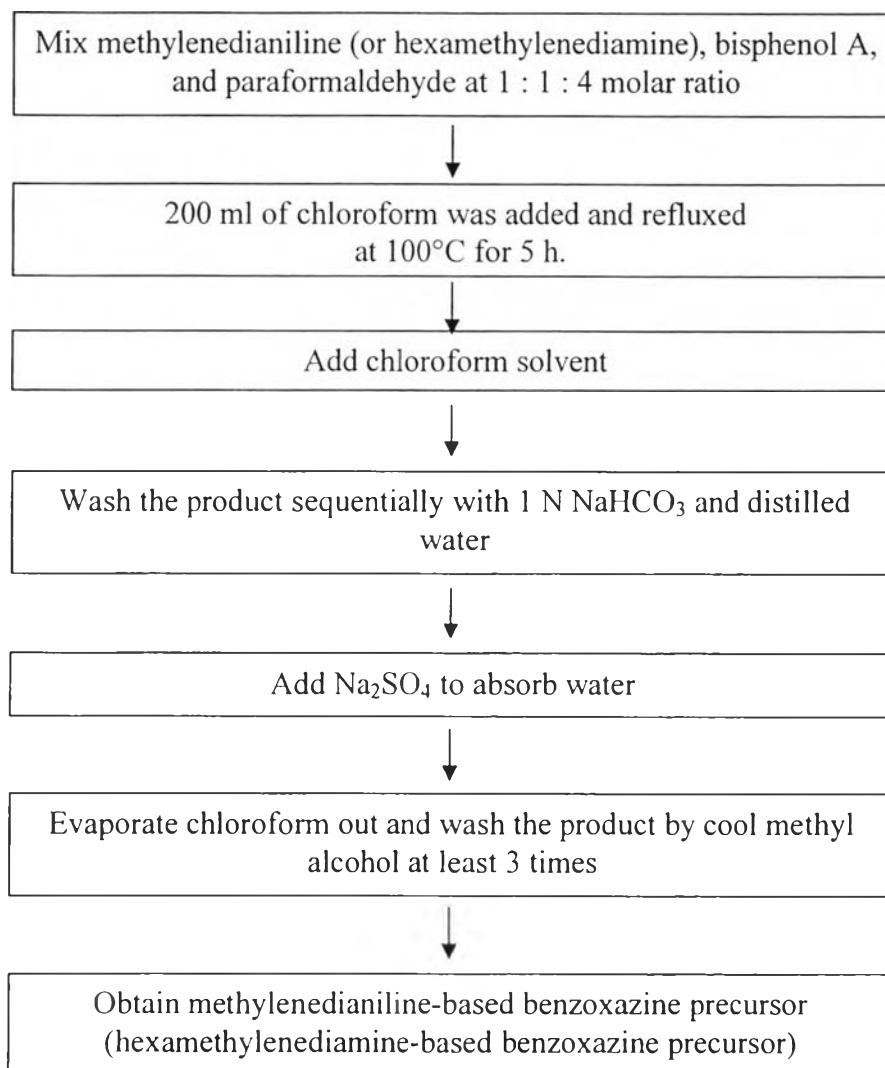
The 5 wt.% of BA-a/PU copolymer at 90/10 vol.% was dissolved in THF. The prepared solution was slowly added dropwise to the stirring BST particle/THF slurry system. Then the mixture was continuously stirred for 1 h. and evaporated THF out at 70°C. Lastly, BA-a/PU copolymer treated BST was dried in a vacuum oven overnight in order to remove the residual solvent.

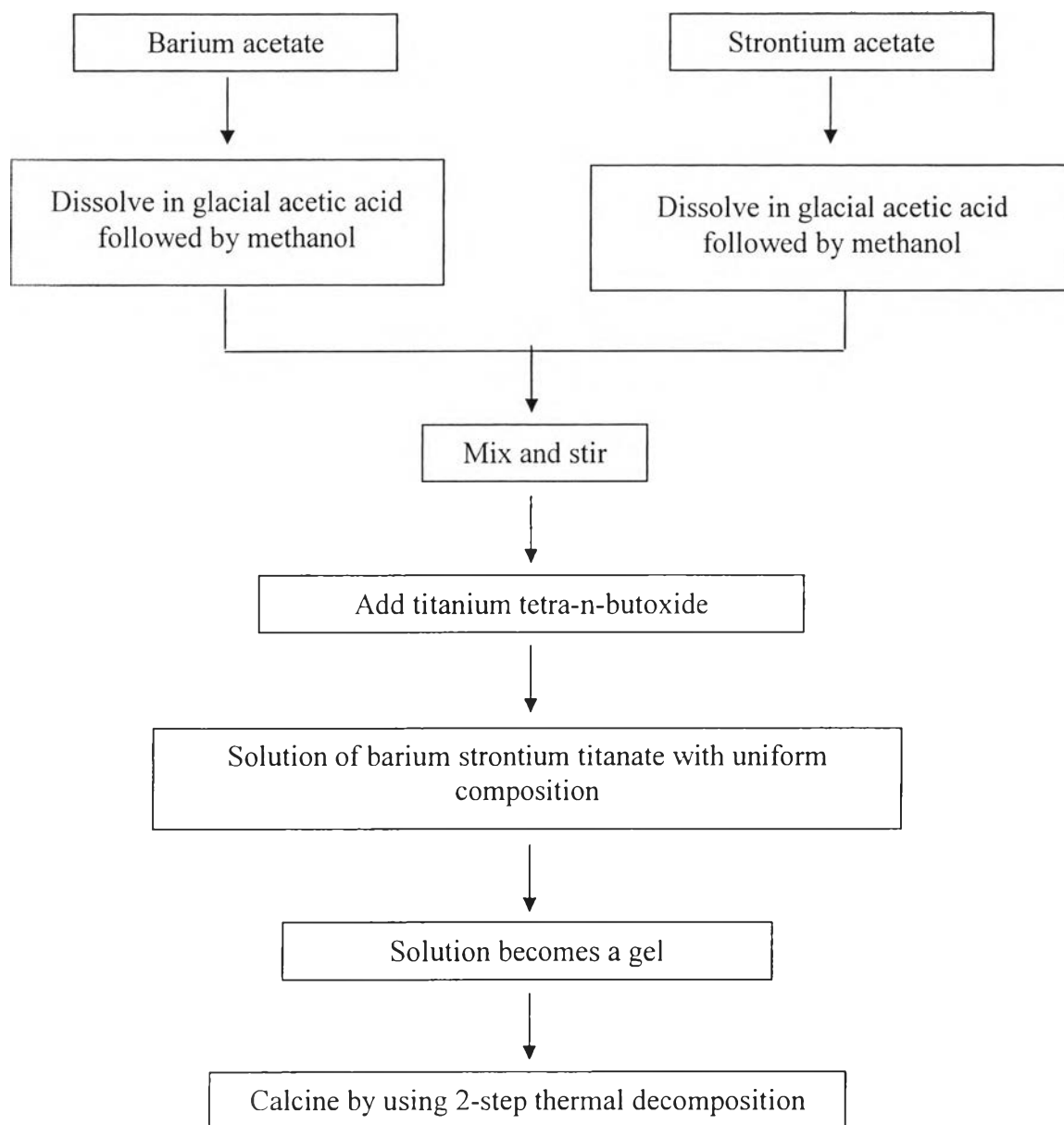
3.2.7.3 *Surface Modification by BA-mda Benzoxazine Precursor*

To modify BST by BA-mda precursor, the same procedure as surface modification by BA-a/PU copolymer was performed, substituting BA-mda in the place of BA-a/PU copolymer.

Schematic 3.1 Aniline-based benzoxazine monomer (BA-a) preparation

Schematic 3.2 Methylenedianiline- (BA-mdm) and hexamethylenediamine-based (BA-hda) benzoxazine precursors preparation



Schematic 3.3 Barium strontium titanate preparation

3.3 Characterization and Testing

3.3.1 X-ray diffractometer (XRD)

XRD was used to observed crystallization of barium strontium titanate. X-ray pattern was measured on X-Ray Diffractometer Model D8 Advance: Bruker AXS, Germany with Cu target at wavelength = 1.5406 angstroms operated at 40 kV. The measurement was 30 mA under Diffrac Plus software of the Bruker Analytical X-ray System XRD Commander as the program used. The sample powder was observed on the 2θ range of 5-70 degree with scan speed 2 degree per minute and increment 0.02 degree.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups related to structure of materials were investigated by using FTIR technique. The FTIR spectra of BST, treated BST powder, benzoxazine based precursors as well as benzoxazine/urethane copolymer were obtained using a Nicolet Nexus 670 FTIR spectrometer in the frequency range of 4000-400 cm^{-1} with 64 scans at a resolution of 2 cm^{-1} . The KBr pellet technique was applied for the sample preparation.

3.3.3 Thermogravimetric Analysis (TGA)

The TGA thermograms were collected using Perkin-Elmer Pyris Diamond TG/DTA instrument. The approximately 5 mg of sample was loaded in the alumina pan and heated from 30 °C to 900 °C at a heating rate of 10 °C/min. under 100 ml/min. of N_2 flow. Degradation temperature of each specimen was investigated at 5%, 10% weight loss whereas char yield as the weight residue at 900°C was reported.

3.3.4 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. Each sample (4-10 mg) was loaded in hermetic aluminum pans with lids. The sample was first heated from 30 °C to 300 °C and then cool down under nitrogen atmosphere with a flow rate of 25 ml/min. The scanning condition was at 5 °C/min.

of heating rate. Finally, the curing profile of benzoxazine based and benzoxazine resin mixtures were obtained.

3.3.5 Scanning Electron Microscope (SEM)

Microstructures of BST powders and the composites were observed using a scanning electron microscope (SEM; HITACHI S-4800) at voltage of 15 kV. Before observed the morphology, the specimens were coated with platinum under vacuum to make them electrically conductive.

3.3.6 Transmission Electron Microscopy (TEM)

Transmission electron microscopy was performed on Hitachi/S-4800 electron microscope with an accelerating voltage of 100 kV was used to determine the particles size of BST powders. The TEM sample was prepared by adding small amount of powder in solvent. The dispersion of the particle was obtained by ultrasonic. The small drop of suspension was placed on a copper grid.

3.3.7 Atomic Force Microscope (AFM)

Atomic force microscope performed on XE-100 Series Park Systems SPM Controller with force modulate mode (FMM) was used to measure Young's modulus and hardness of each region of copolymers which can be referred to the distribution of urethane content in benzoxazine phase. In this mode, at 15 μm of scan size and 0.5 Hz of scan rate were set so as to analysis the mechanical in the microstructure level of materials.

3.3.8 Nuclear Magnetic Resonance Spectrometer (NMR)

The ^1H -NMR was used to confirm molecular structure of materials. The spectra was recorded on a Varian Mercury NMR spectrometer operated at 400.00 MHz by using deuterated chloroform (CDCl_3) as a solvent to which the chemical shifts (δ) was given.

3.3.9 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties and relaxation behaviors of the specimens were measured by GABO EPLEXOR 100 N. The dimension of specimens was 10 mm \times 40 mm \times 1 mm. The test was performed in tension and three-point

bending modes. In a temperature sweep experiment, 1 Hz of frequency and 0.1% of strain value were applied. The temperature was scanned from -100 °C to 250 °C for benzoxazine/urethane alloys (BA-a/PU) and 25 °C to 250 °C for high molecular weight polybenzoxazines and the BA-a/PU polymer composites with a heating rate of 2 °C/min under nitrogen atmosphere.

3.3.10 Analytical balance with density kit

The apparatus equipped with Balance SARTORIUS research RC210S and kit SARTORIUS YDK201. Relative density of materials was measured by following the test method A of ASTM D 792-00. The dimension of samples was 20 mm × 5 mm × 2 mm. To determine the density, the specimen was weighed in air and then weighed when it was completely immersed in deionized water. The weight was again noted after the sample was removed and wiped of excess water. The density of the specimen was finally obtained by calculation. Three times of analysis were averaged to achieve the final density.

3.3.11 Agilent E4991A RF Impedance/Material Analyzer

Dielectric properties [dielectric constant (ϵ'), and loss tangent ($\tan \delta$; ϵ''/ϵ')] were determined by using an E4991A RF impedance/material analyzer equipped with a 16453A dielectric material test fixture, Agilent Technologies, Inc., USA). The scan frequencies ranged from 300 MHz to 1 GHz. The prepared sample was placed inside a Espec SU-261 temperature chamber (variable temperature oven) and temperature was controlled from -50 °C to 150 °C. First, the sample was heated from room temperature to 150 °C and then cooled down by 10 °C increment until reaching -50 °C. During the temperature ramp down, data collection was delayed for 2 min. at each temperature constant in order to increase the accuracy of the dielectric measurement.

3.3.12 Gas Pycnometer

The density of BST powder and polybenzoxazine and poly(benzoxazine/urethane) based were measured by pycnometer (Quantachrome, Ultrapycnometer 1000) under helium purge at pressure of 20 psi.