



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Paraformaldehyde (98.7%) was purchased from Merck. Aniline was purchased from Panreac. Glacial acetic acid, chloroform, tetrahydrofuran, methyl alcohol, sodium hydroxide and barium acetate were purchased from Lab Scan. Strontium acetate hydrate (99.995%), hexafluorobisphenol A, phthalocyanine and 3-aminopropyl trimethoxy silane were purchased from Fluka. Titanium tetra-n-butoxide (97%) was purchased from Aldrich. All chemicals were used without further purification.

### 3.2 Equipments

#### 3.2.1 Proton and Fluorine Nuclear Magnetic Resonance Spectrometer

##### (<sup>1</sup>H NMR and <sup>19</sup>F NMR)

<sup>1</sup>H NMR and <sup>19</sup>F NMR spectrometer was used to confirm the chemical structure of aniline based and fluorinate based benzoxazine monomer. The <sup>1</sup>H NMR spectra was recorded on Bruker Avance DPS-400 and deuterated chloroform was used as solvent.

#### 3.2.2 Fourier Transformation Infrared Spectroscopy (FTIR)

Functional groups of benzoxazine monomer were measured by a fourier transformation infrared spectrophotometer (NEXUS 670 FTIR). All spectra were recorded with absorbance mode in the wave number range of 4000-400 cm<sup>-1</sup> and 32 scans per resolution.

#### 3.2.3 Differential Scanning Calorimeter (DSC7)

A heating profile of benzoxazine monomer was performed by a differential scanning calorimeter 7, DSC 7 (Perkin Elmer). The samples were heated from 30-300 °C at a heating rate of 10 °C/min under N<sub>2</sub> purge.

### 3.2.4 Dynamic Mechanical Analysis (DMA)

Glass transition temperature ( $T_g$ ) of poly benzoxazine was measured by NETZSCH DMA 242 operated at 1 Hz under  $N_2$  with flow rate of 100 ml/min.

### 3.2.5 X-ray Diffraction (XRD)

A crystal phase and structure of BST powders was analyzed by X-ray diffraction (Rigaku, model Dmax 2002) with Ni-filtered  $CuK\alpha$  radiation operated at 40 kV and 30 mA with scan speed 5.00 deg/min from the  $2\theta$  range of 5.00 to 90.00 degree.

### 3.2.6 Scanning Electron Microscope (SEM)

Microstructures and surface morphology of BST powders and the composites were observed by a scanning electron microscope (SEM; JSM-5200, Jeol) at voltage of 15 kV.

### 3.2.7 Transmission Electron Microscope (TEM)

Transmission electron microscope (TEM; H-7650, Hitachi) was used to observe particle size of sol-gel BST powders.

### 3.2.8 Pycnometer

The apparent density of BST powders and benzoxazine monomer were measured by pycnometer (Quantachrome, Ultrapycnometer 1000) under helium purge at pressure of 20 psi.

### 3.2.9 Impedance/Gain-Phase Analyzer

Dielectric measurement of composites was performed with Hewlett-Packard 4194A Impedance/Gain-Phase Analyzer in parallel capacitance ( $C_p$ ) mode, with frequency from 1 kHz to 10 MHz at room temperature. The dielectric constant ( $\epsilon$ ) of the composites was calculated from the measured thickness and capacitance by using the following equation:

$$\epsilon = \frac{Cd}{\epsilon_0 A}$$

where  $C$  is the capacitance (F),  $\epsilon_0$  is the free space dielectric constant value ( $8.85 \times 10^{-12}$  F/m),  $A$  is the capacitor area ( $m^2$ ), and  $d$  is the thickness of specimen (m).

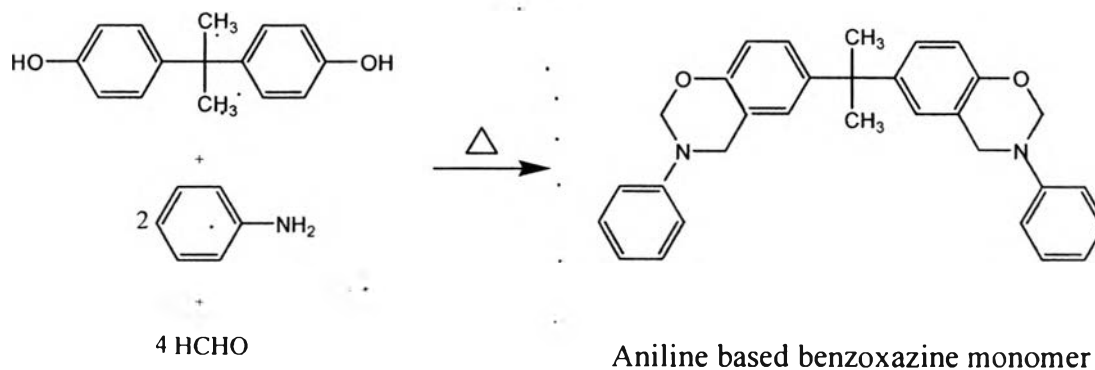
### 3.2.10 Compression Molding Machine

Polybenzoxazine and composite samples were performed by a compression press (Lab Tech, model LP 20).

### 3.3 Methodology

#### 3.3.1 Aniline Based Benzoxazine Monomer Preparation

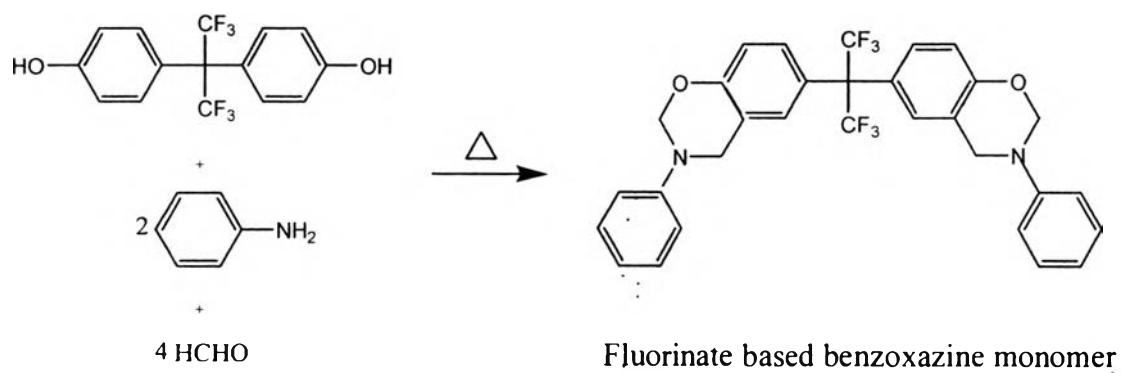
The synthesis of aniline based benzoxazine monomer is based on the reaction of bisphenol A, paraformaldehyde, and aniline at the molar ratio of 1:4:2 respectively, as shown in Figure 3.1. For this experiment, the monomer was prepared from solventless method; the starting materials were mixed together without solvent at temperature of 100°C for 30 min. Then the product with high yellow viscous liquid was obtained. This viscous product was dissolved in chloroform and washed sequentially with 0.1 N NaOH and water for three times to eliminate any unreacted formaldehyde and dried over Na<sub>2</sub>SO<sub>4</sub>. The chloroform was then removed with a rotary evaporator and the solid products were washed by cool methyl alcohol at least three times to obtain white powder benzoxazine monomer.



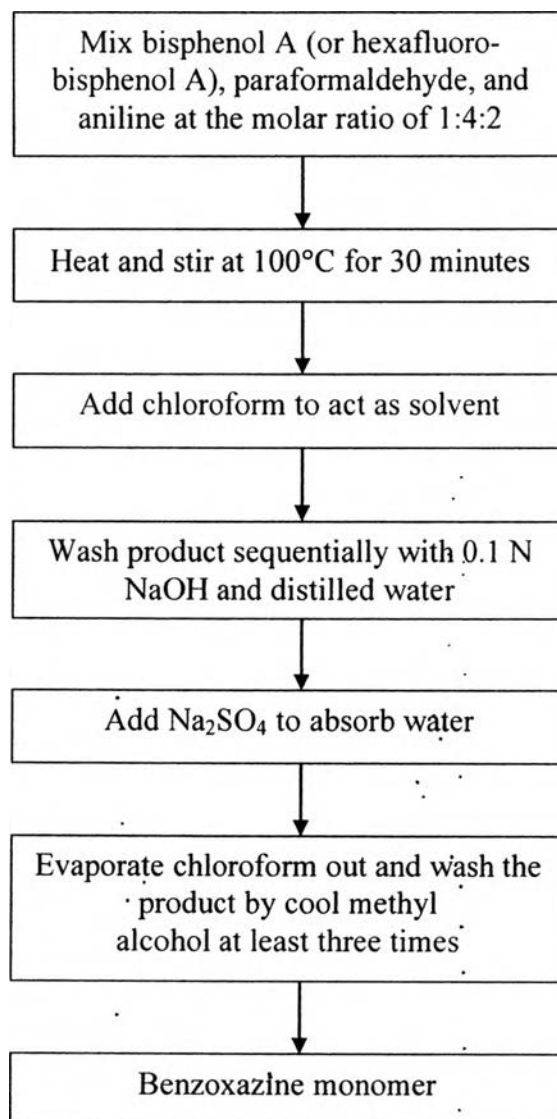
**Figure 3.1** Synthesis reaction of benzoxazine monomer based on bisphenol A, aniline and paraformaldehyde.

### 3.3.2 Fluorinate Based Benzoxazine Monomer Preparation

The fluorinate based benzoxazine monomer was prepared by the reaction of hexafluorobisphenol A, paraformaldehyde, and aniline at a molar ratio of 1:4:2, respectively, with the same procedure as aniline based monomer.



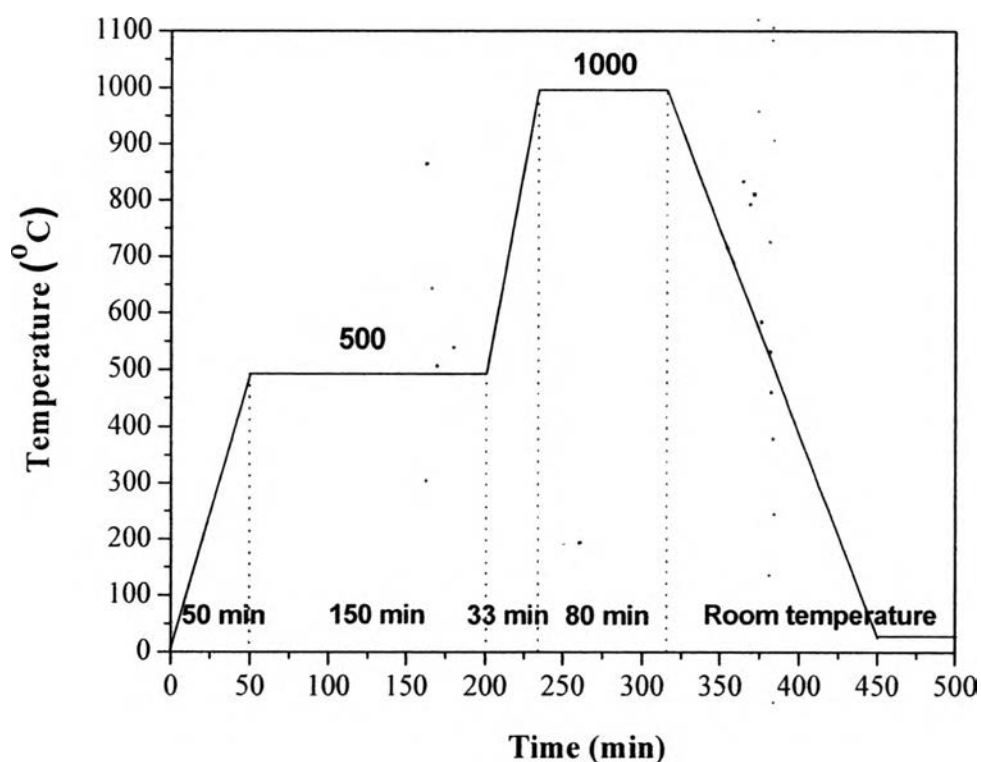
**Figure 3.2** Synthesis reaction of benzoxazine monomer based on hexafluorobisphenol A, aniline and paraformaldehyde.



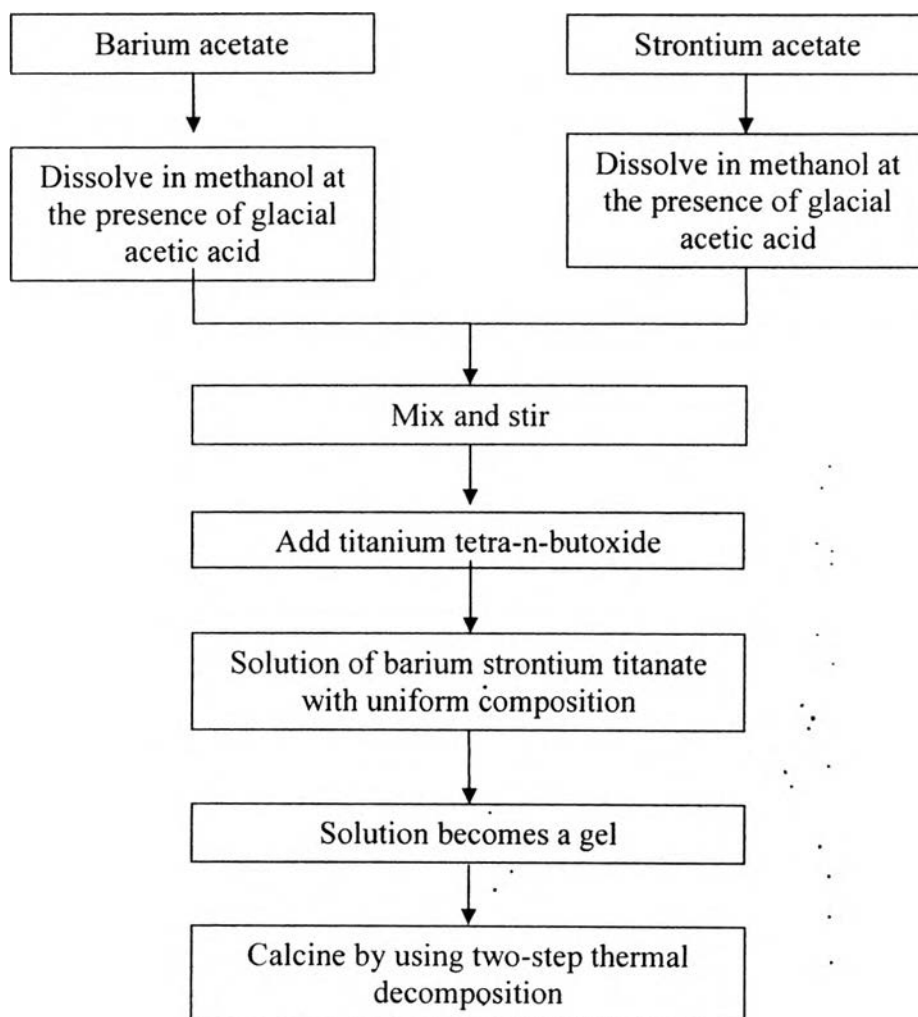
**Figure 3.3** Benzoxazine monomer preparation.

### 3.3.3 Preparation of Barium Strontium Titante by Sol-Gel Process

Barium strontium titante ( $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ ) was prepared by dissolving 0.3 mole of barium acetate and 0.7 mole of strontium acetate separately in acetic acid, followed by the addition of methanol to each one. The solutions were then mixed and stirred to obtain a clear solution. Then an equimolar amount of titanium (iv) n-butoxide was added into this mixture under vigorous stirring. When the solution became a gel, it was calcined by using 2-step thermal decomposition to decompose the solvent and crystallize  $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$  powders.



**Figure 3.4** Temperature program for the 2-step thermal decomposition.



**Figure 3.5** Barium strontium titanate preparation.

### 3.3.3 Surface Modification of BST Powders

#### 3.3.3.1 *Surface Modification by Silane Coupling*

3-aminopropyl-trimethoxysilane (1g) was dissolved in water/ethanol (5ml/95ml) and the solution was then mixed with BST powder (40 g). This suspension was ultrasonicated at room temperature for 10 min and stirred at 70°C for 1 h. The treated suspension was centrifuged and subsequently washed by ethanol and dried in a vacuum oven at 50°C. Finally, the coupling agent modified BST particles were obtained.

#### 3.3.3.2 *Surface Modification by Benzoxazine Monomer*

In this method the various thicknesses of benzoxazine coating on BST powders were obtained by varying the benzoxazine solution concentration at 1wt%, 3wt%, and 5wt% in THF. The solution was slowly added dropwise to stirring BST particle/THF slurry. Then the mixture was stirred for 1 hr and evaporated THF out at about 70 °C. Lastly, treated BST was dried in a vacuum oven overnight in order to remove residual solvent.

#### 3.3.3.2 *Surface Modification by Phthalocyanine*

0.1 wt% of phthalocyanine powder was dissolved in DMAc solvent then added the solution into stirring BST particle/DMAc slurry. The mixture was then stirred for 1 hr and evaporated DMAc out at 200°C. After that the residual solvent was removed again by drying in a vacuum oven overnight.



### 3.3.4 Composite Preparation

In this part, the composite of aniline based polybenzoxazine and BST ceramic ( $Ba_{0.3}Sr_{0.7}TiO_3$ ) was fabricated. Due to the much difference between the density of aniline based benzoxazine monomer and BST powder, the monomer and BST powder with 30, 50 and 80 wt% were firstly mixed together by melt mixing method to prevent the separation between two phases after fabrication step. Then the mixtures were fabricated as the composite specimens with the thickness of 1.5 mm and 15 mm in diameter by compression molding with the curing conditions given in Table 3.1.

**Table 3.1** Temperature program for compression molding process

Temperature (°C)	Time (min)	Applied load (0.25 ton)
120	15	-
140	15	-
160	15	-
180	30	+
200	30	+
230	60	+