CHAPTER III

EXPERIMENTAL

3.1 Materials and Instruments

Chemical reagents

- Paraformaldehyde 98.7% (Merck.)
- Bisphenol A
- Hexafluorobisphenol A (Fluka)
- Aniline (Panreac.)
- Glacial acetic acid (Lab scan)
- Chloroform (Lab scan)
- Tetrahydrofuran (Lab scan)
- Methyl alcohol (Lab scan)
- Sodium hydroxide (Lab scan)
- Barium acetate (Lab scan)
- Strontium acetate hydrate 99.995% (Fluka)
- Titanium tetra-n-butoxide 97% (Aldrich)
- 3-aminopropyl trimethoxy silane (Fluka)
- Pthalocyanine (Fluka)

Apparatus and glass wares

- Beaker glass
- Cylinder glass
- Mechanical stirrer
- Glass syringe
- Desiccators
- Spatulas
- Watch glasses
- Droppers
- Funnels
- Filter flasks

3.2 Chemical Synthesis and Composite Preparation

3.2.1 Synthesis of Aniline Based Benzoxazine Monomer

The preparation 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 and for this experiment, the monomer was prepare by 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 Sodium hydroxide (NaOH) and water for 3 times to eliminate any unreacted formaldehyde and dried over sodium sulfate (Na_2SO_4). Then use the chloroform to remove with a rotary evaporation and the solid products were washed by cool methyl alcohol at least 3 times to obtain the white powder benzoxazine monomer.

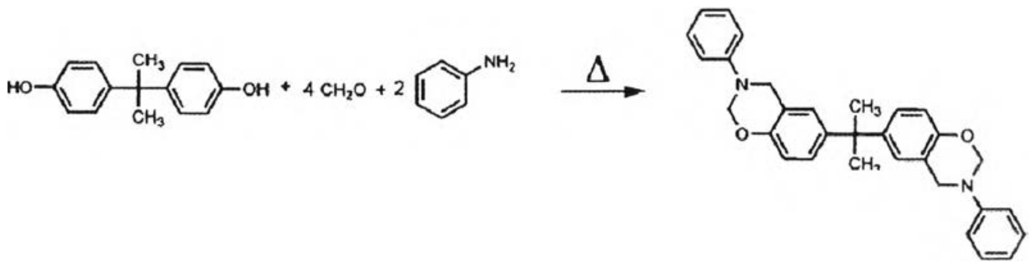


Figure 3.1 Synthesis of aniline-based benzoxazine (Ghosh *et al.*, 2007).

3.2.2 Synthesis of Fluorinate Based Benzoxazine Monomer

The same procedure as aniline based monomer to prepare the fluorinate based benzoxazine monomer was followed. The starting chemicals, hexafluorobisphenol A, paraformaldehyde, and aniline were prepared at molar ratio of 1:4:2, as shown in Figure 3.2.

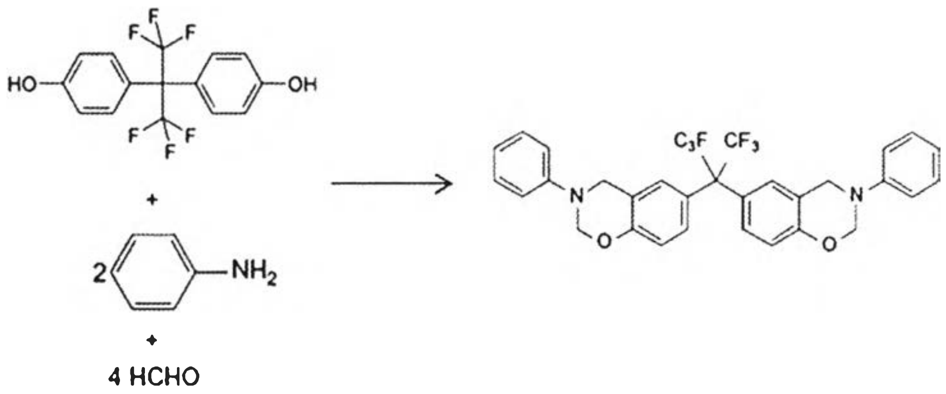


Figure 3.2 Synthesis of fluorinate-based benzoxazine (Su *et al.*, 2003).

3.2.3 Preparation of Barium Strontium Titanate by Sol-Gel Process

Barium strontium titanate ($Ba_{0.3}Sr_{0.7}TiO_3$) 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 methyl alcohol to each one. The solution were then mixed and stirred to obtain a clear solution. Then an equimolar amount of titanium n-butoxide was added into this mixture under vigorous stirring. When the solution became a gel, it was 4calcined by using 2-step thermal decomposition to decompose the solvent and crystallize $Ba_{0.3}Sr_{0.7}TiO_3$ powders are shown in Figure 3.3.

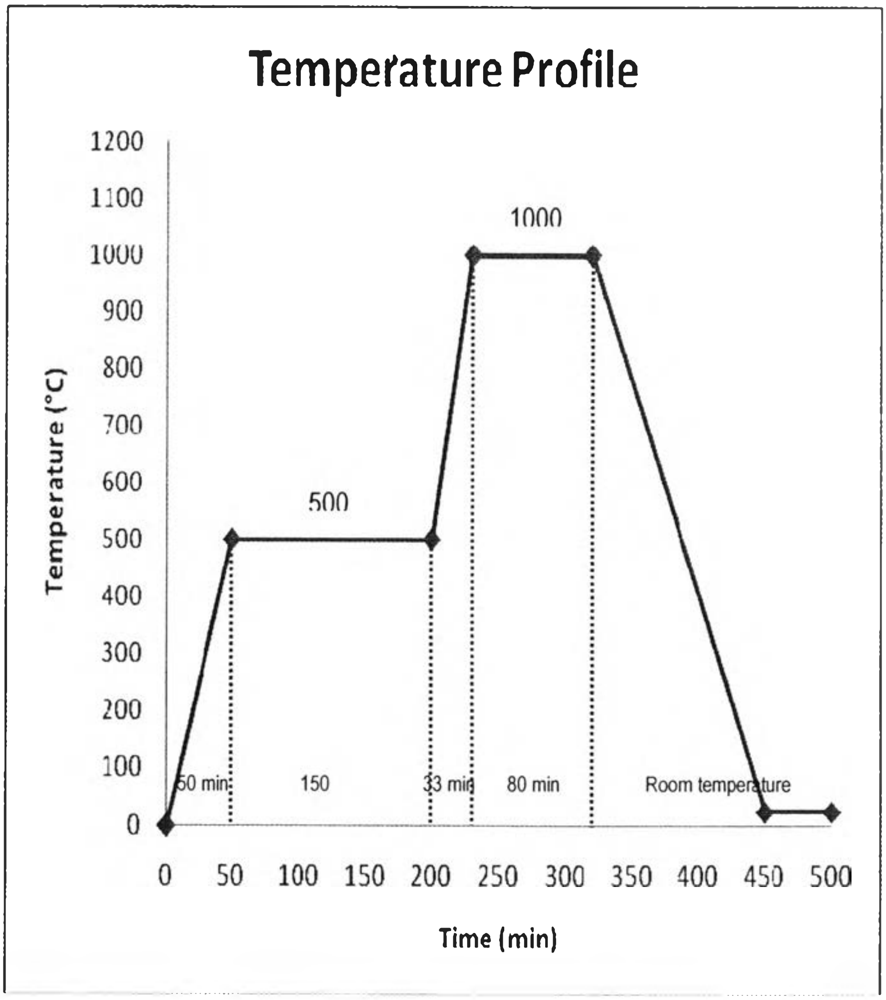


Figure 3.3 The Temperature profile for two-step thermal decomposition of BST.

3.2.4 Surface Modification of BST Powder

3.2.4.1 Surface Modification by Silane Coupling

Dissolve the 3-aminopropyl-trimethoxysilane 1 g. in water 5 ml: ethanol 95 ml solution then mixed that solution with BST powders 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

3.2.4.2 Surface Modification by Benzoxazine Monomer

Dissolve 5wt% of aniline based benzoxazine monomer in THF. The solution was slowly added drop wise to stirring BST particle/THF slurry. Then the mixture was stirred for 1 h. and evaporated THF out at about 70°C. Lastly, treated BST was dried in a vacuum oven overnight in order to remove the residual solvent.

3.2.4.3 Surface Modification by Phthalocyanine

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

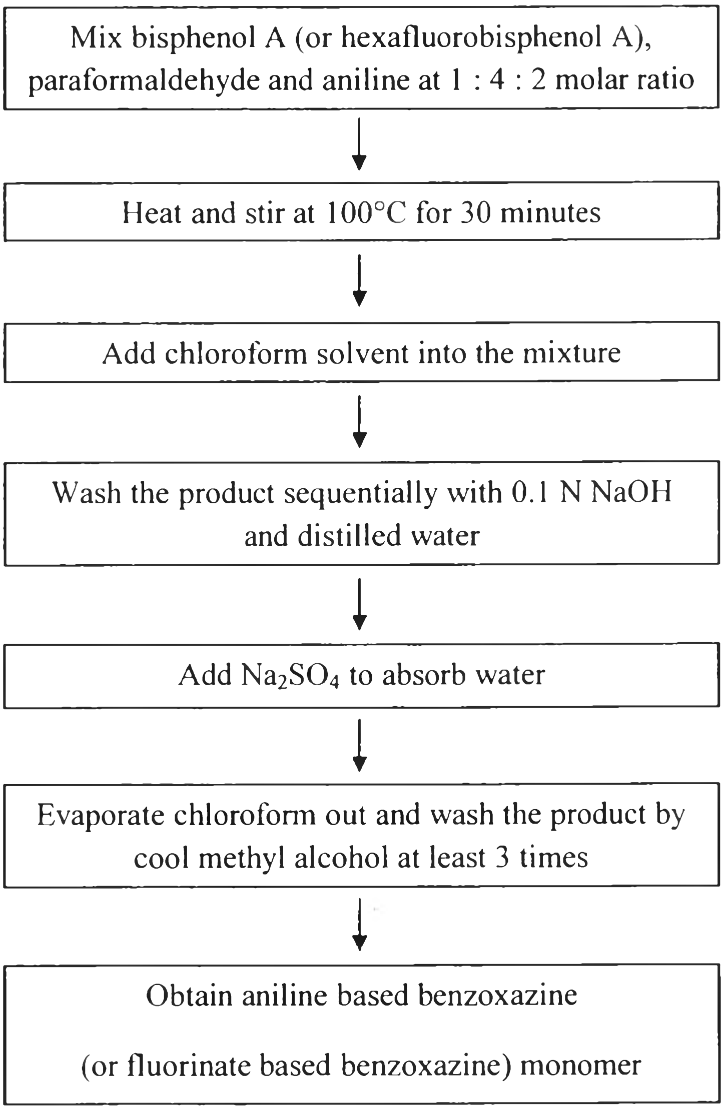
3.2.5 Composite Preparation

The composite between polybenzoxazine based and BST ceramic ($Ba_{0.3}Sr_{0.7}TiO_3$) were prepared. Owing to the much difference between the densities of 2 substrate, then mix the benzoxazine monomer and BST powder with 30, 40, 50, 60, 70 and 80 wt% by melt mixing process to prevent the separation of 2 phases. After that, the mixtures was fabricated as composite specimens with the thickness of 1.2 mm. and 2.0 mm in diameter by compression molding with curing conditions which given in Table 3.1.

Table 3.1 Temperature profile for compression molding process

Temperature (°C)	Time (minute)	Applied load (150 kg.)
120	30	-
140	30	-
160	30	-
180	30	-
200	30	+
230	60	+

Flow chart of benzoxazine monomer preparation



Mix bisphenol A (or hexafluorobisphenol A), paraformaldehyde and aniline at 1 : 4 : 2 molar ratio

Heat and stir at 100°C for 30 minutes

Add chloroform solvent into the mixture

Wash the product sequentially with 0.1 N NaOH and distilled water

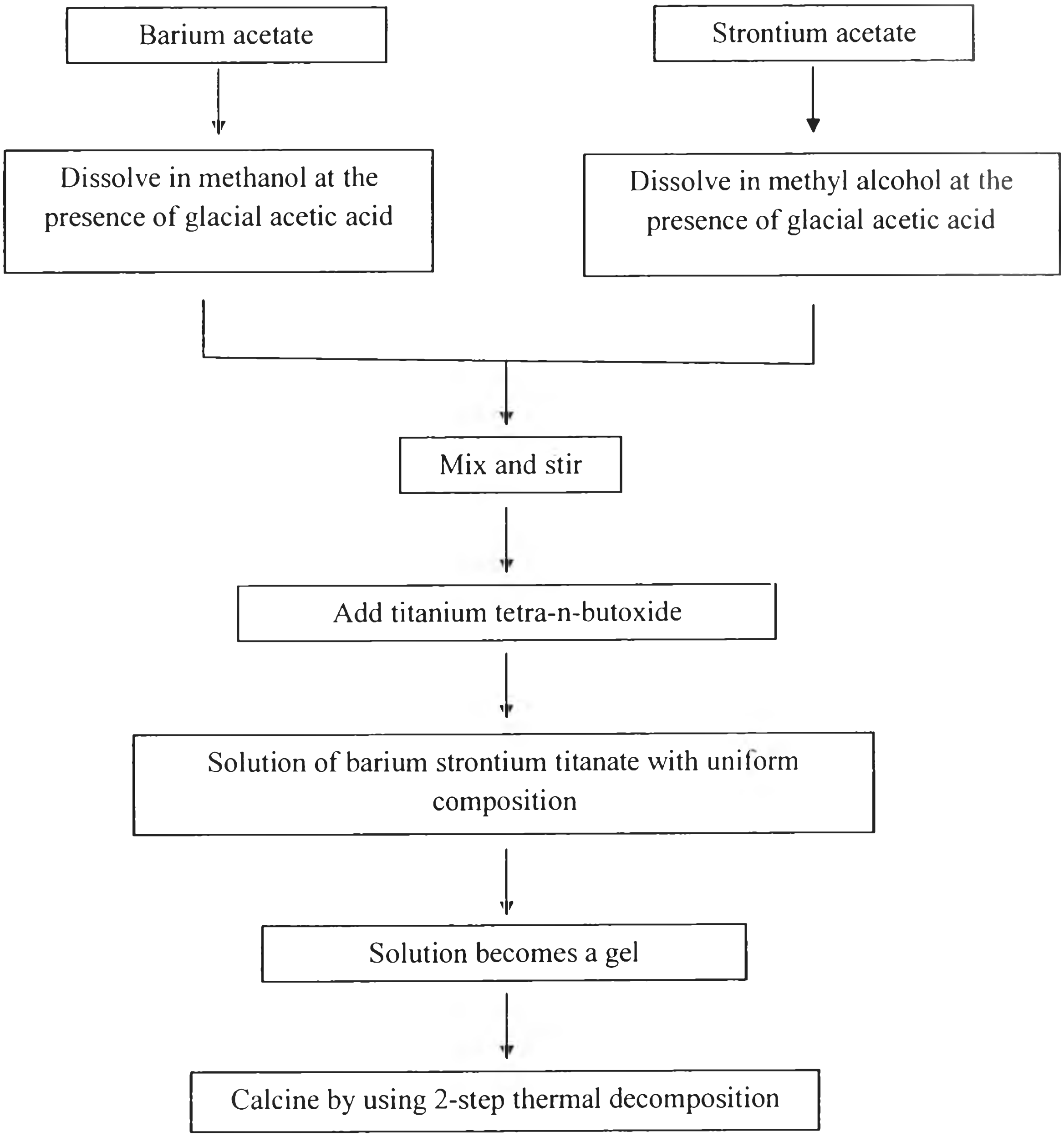
Add Na_2SO_4 to absorb water

Evaporate chloroform out and wash the product by cool methyl alcohol at least 3 times

Obtain aniline based benzoxazine

(or fluorinate based benzoxazine) monomer

Flow chart of barium strontium titanate preparation



3.3 Characterization and Testing

3.3.1 Proton and Fluorine Nuclear Magnetic Resonance Spectrometer (^{1}H NMR and ^{19}F NMR)

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

3.3.2 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 400-4000 cm^{-1} and 32 scans per resolution.

3.3.3 Differential Scanning Calorimeter (DSC 7)

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_2 purge.

3.3.4 Dynamic Mechanical Analysis (DMA)

Glass transition temperature (Tg) of polybenzoxazine was measured by GABO EPLEXOR 100 N operated at 1 Hz under N_2 with flow rate of 100 ml/min.

3.3.5 X-ray Diffraction (XRD)

A crystal phase and structure of BST powders was analyzed by X-ray differaction (Rigaku, model Dmax 2002) with Ni-filteref CuKα radiation operated at 40 kV and 30 mA with scan speed 5.00 deg/min from the 2Θ range of 5.00 - 90.00 degree.

3.3.6 Scanning Electron Microscope (SEM)

Microstructure and surface morphology of BST powders and the composite were observed by a scanning electron microscope (SEM; HITACHI S-4800) at voltage of 15 kV.

3.3.7 Thermal gravimetric analysis (TGA)

Residual weight and decomposition temperature of the Polybenzoxazine and the composite was measured by Perkin Elmer Pyris Diamond TG/DTA instrument by using the platinum pan for reference and operated the heat from 30 °C to 900°C and heating rate of 10°C/mins. This condition is flow under N_2 with flow rate of 100 ml/min

3.3.8 Transmission Electron Microscope (TEM)

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

3.3.9 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.

3.3.10 Compression Molding Machine

Polybenzoxazine and composite samples were performed by a Compression Press (Lab Tech, model LP 20) in curing step conditions that given in Table 3.1.

3.3.11 Agilent E4980A LCR meter

Dielectric measurement of composite was preformed with Agilent E4980A Impedance/Gain-Phase Analyzer in parallel capacitance (C_p) mode, with frequency from 20 Hz to 2 MHz at room temperature. The dielectric constant (ε) of the composites was calculated from the measured thickness and capacitance by using the following equation:

$$\varepsilon = \frac{Cd}{\varepsilon_0 A}$$

where C is the capacitance (F), ε_0 is the free space dielectric constant value (8.85×10^{-12} F/m), A is the capacitor area (m^2), and d is the thickness of specimen (m).

3.3.12 Agilent E4991A RF Impedance/Material Analyzer

Microwave dielectric properties of composite were performed with Agilent E4911A Network Analyzers with frequency from 1 MHz to 1 GHz and temperature from -50 to 150°C with SU-261 Bench-top Type temperature and humidity chamber.