



## CHAPTER III METHODOLOGY

### 3.1 Materials and Instruments

#### 3.1.1 Materials

The poly(vinylidene fluoride) (PVDF) powder(#1008) material was kindly supported by Solvay (Thailand) Limited. Glacial acetic acid and methyl alcohol were purchased from Italmar. The Poly(vinylidene fluoride) (PVDF) pellets were given by Solvay (#1008). Barium acetate and *N,N*-Dimethyl formamide (DMF) and were purchased from Lab Scan. Strontium acetate (99.995%) and titanium tetra-*n*-butoxide (97%) were purchased from S.M. Chemical. All chemicals are used without further purification.

#### 3.1.2 Instruments

- FTIR Spectrometer (Nicolet/Nexus:670)
- Scanning Electron Microscope (SEM) (JEOL, LS002)
- X-ray diffraction (Rigaku, model Dmax 2002)
- Particle Size Analyzer (PSA) (Mastersizer, X)
- Thermogravimetric Analyzer, (Q50 TGA)
- Differential Scanning Calorimeter, DSC7 (Perkin Elmer)
- Impedance/Gain-Phase Analyzer (Hewlett Packard., model 4194A)
- LCR meter (Agilent., model E4980A)
- Transmission Electron Microscope (TEM) (JEOL, model MJEM-1230)
- RT66A (Ferroelectric Measurement Test System)
- $d_{33}$  meter (APC Int. Ltd., model 8000)
- Compression Molding Machine (Labtech, model LP 20)

## 3.2 Methodology

### 3.2.1 PVDF Film Preparation

Poly(vinylidene fluoride) pellets manufactured from Solvay Company (Belgium) (Solef 1008) were used. The fabrications of PVDF film was done by the solution casting which PVDF pellets were dissolved in DMF solution. The viscous solution was then casted on glass substrate. After the solvent evaporation in a stove at 60°C for 1 hour under vacuum, the sample films of 70-90 μm thickness were obtained.

#### 3.2.1.1 *Stretching of PVDF Film*

PVDF film from casting technique was stretched by mechanical testing machine (Universal testing machine, Lloyd) at 90°C to obtain film at different stretching ratio at constant stretching rate of 50 mm/min. The stretching ratio was calculated by the following equation:

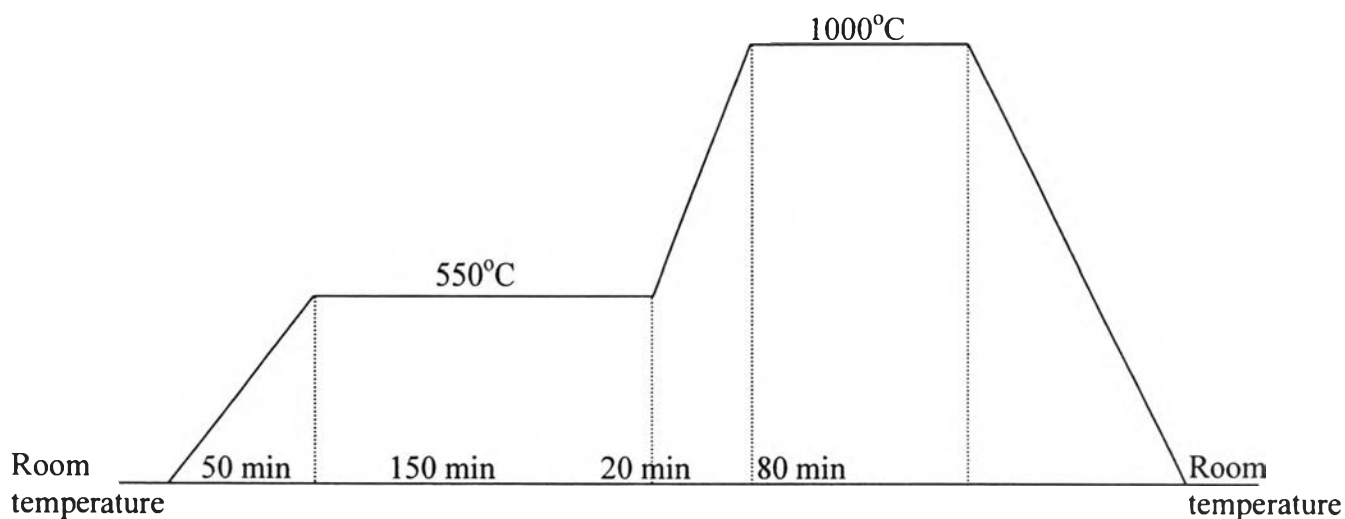
$$\text{Stretching ratio} = \frac{\text{Final length}}{\text{Initial length}}$$

### 3.2.2 Composite Film Preparation

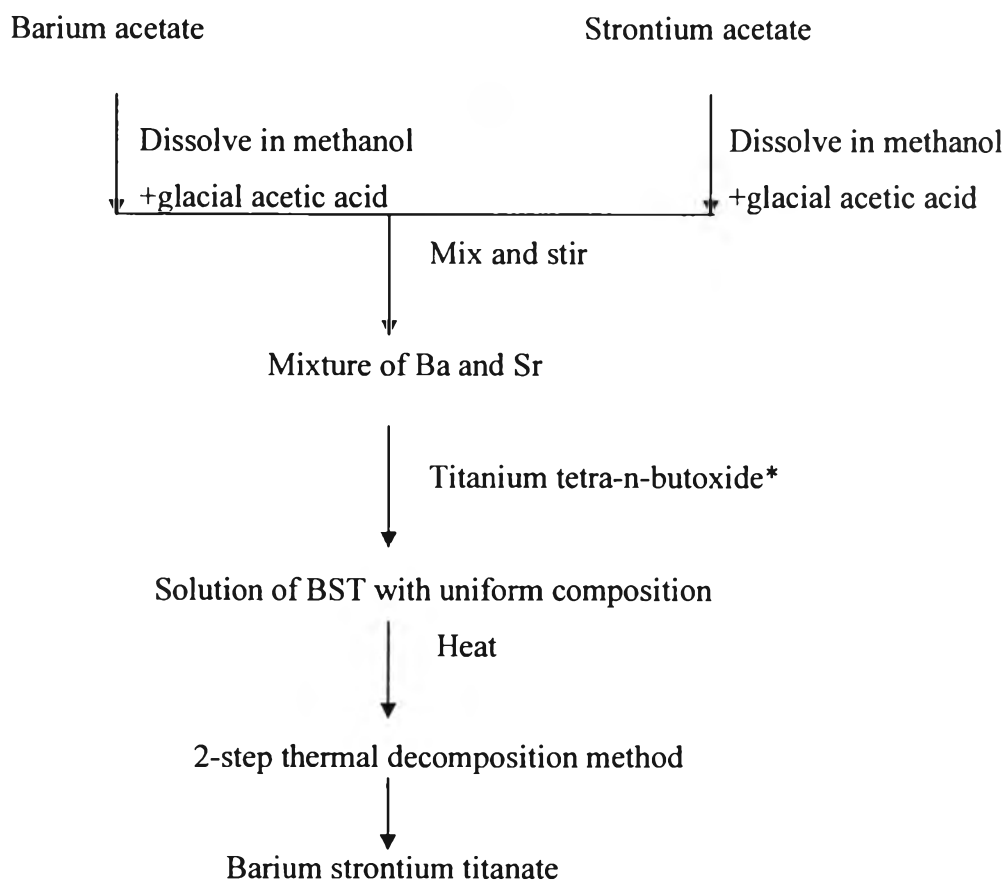
#### 3.2.2.1 *Synthesis of Barium Strontium Titanate (BST)*

Ba<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub> powder was prepared by sol-gel process. Equal moles of barium acetate and strontium acetate were dissolved separately into methyl alcohol 20 ml in the presence of glacial acetic acid 10 ml. The solutions were then mixed and stirred for 20 minutes at room temperature. The prescribed amount of titanium-n-butoxide was added into the mixture. All the materials mentioned above were thoroughly mixed to prepare a stable solution with uniform composition until gel solution occurs. After that the gel solution was poured into an alumina crucible and heated by using a 2-step thermal decomposition method in order to decompose the precursors and to crystallize the barium strontium titanate and investigate the dielectric properties of composites.

## 3.2.2.2 Ceramic Processing



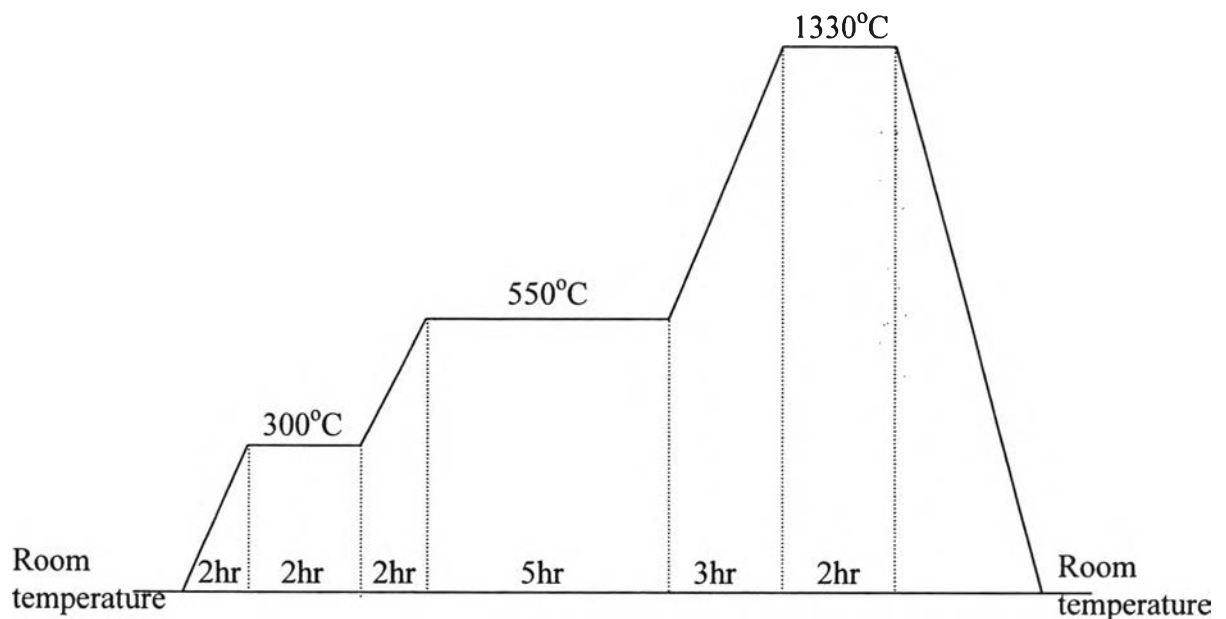
**Figure 3.1** Temperature program for the 2-step thermal decomposition method.



**Figure 3.2** Barium Strontium Titanate Preparation.

### 3.2.2.3 Ceramic Pellet Preparation

Polyvinyl alcohol (PVA) was weighed (4% by weight of BST powder) then dissolved it into acetone. After that, this solution was poured into ceramic powders and stirred until a homogeneous slurry material was obtained. Then this slurry material was left overnight under air, followed by grinding and sieving to obtain the powder. Then the powders were pressed in a press form by using a force of around 7-8 tons and a sintering process was performed by putting the ceramic pellets into an oven by using the following temperature program as shown in Figure 3.3 in order to obtain a sintered product for electrical measurement.



**Figure 3.3** Temperature program for the sintering process of ceramic pellet.

### 3.2.2.4 PVDF-Barium Strontium Titante (BST) Composite Preparation

PVDF powder supplied by Solvay (Solef 1008) was dissolved in dimethyl formamide (DMF) at 60°C. For composite preparation, the polymer:solvent ratio was 1:10 w/v. Proportionate quantity of  $Ba_{0.7}Sr_{0.3}TiO_3$  powder was added in the polymer solution. It was homogenized by magnetic stirrer. Additional mixing by ultrasonic was used to guarantee that the powder agglomeration was broken. The composite film was prepared by a Labtech compression as pressing dried solution at 180°C for 20 minutes under pressure of 10 tons. Following the two

methods above, the composite films of 20%, 40%, and 60% by weight ceramic were fabricated.

### 3.2.3 Laminated Film Preparation

From this method, PVDF/PVDF-BST bilayer films, PVDF-PVDF/BST-PVDF trilayer films and PVDF/BST-PVDF-PVDF/BST trilayer films were fabricated by Labtech compression machine. They were compressed at 90°C for 20 min under pressure 10 tons.

### 3.2.4 Piezoelectric Induction in Material

In order to induce piezoelectric response to the material, PVDF film were subjected to large and enduring electric fields (for typical poling conditions, the electric field is approximately 50 kV/cm). And all laminate samples were poled by using corona discharge with 15 kV and 0.007 mA.

## 3.3 Characterization and Testing

### 3.3.1 Fourier Transformation Infrared Spectroscopy (FTIR)

The Crystalline of PVDF was measured by a Fourier Transformation Infrared Spectrophotometer (FTIR). The measurement was made in absorbance mode using a Bruker FTIR Spectrometer, model Vector 3.0, using 32 scans per resolution. Thus, for a system containing  $\alpha$  and  $\beta$  phase the relative fraction of the  $\beta$  phase,  $F(\beta)$ , was calculated by the following equation:

$$F(\beta) = \frac{X_{\beta}}{X_{\alpha} + X_{\beta}} = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}}$$

Where  $X_{\alpha}$  and  $X_{\beta}$  are the degree of crystallinity of  $\alpha$  and  $\beta$  phases,  $A_{\alpha}$  and  $A_{\beta}$  are the absorbances of  $\alpha$  and  $\beta$  phases at 763 and 840  $\text{cm}^{-1}$ , respectively.

ATR measurements can be at best used to analyze the dense selective side of membranes, while the optical interfacing of the ATR crystal when a very rough surface is present.

### 3.3.2 X-ray Diffraction (XRD)

A crystal phase and structure of laminated PVDF film were analyzed by X-ray diffraction (Rigaku, model Dmax 2002) with Ni-filtered CuK $\alpha$  radiation operated at 40 kV and 30 mA.

### 3.3.3 Differential Scanning Calorimeter (DSC7)

Heating profiles of PVDF film and all stretched film were performed by a differential scanning calorimeter 7, DSC 7 (Perkin Elmer) at a heating rate of 10 °C/min. The samples were heated from 30°C to 300°C. Different scanning calorimetry (DSC) was used to determine the crystallization temperature for the dynamic phase diagram. The degree of crystallinity was measured as the ratio between  $\Delta H_m$  and  $\Delta H_0$ , as following equation

$$\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_0} \times 100 \quad (3)$$

where  $\Delta H_m$  is the melting enthalpy of the material under study and  $\Delta H_0$  is the melting enthalpy of totally crystalline material ( $\Delta H_0 = 104.50$  J/g for PVDF).

### 3.3.4 Thermogravimetric Analysis (TGA)

Thermal degradation was performed by a high resolution TG-DTA Pyris Diamond (Perkin Elmer). Samples were loaded on a the alumina pan heated from 50°C to 1150°C with a heating rate of 20°C/min under N<sub>2</sub> flow.

### 3.3.5 Scanning Electron Microscope (SEM)

The structure and morphology on surface, cross-sections of film were observed by scanning electron microscopy (SEM). The film samples are gold sputtered and analyzed by using a scanning electron microscope (JEOL, model LS002).

### 3.3.6 Pycnometer

The apparent density of PVDF and laminated PVDF film were measured by pycnometer (Quantachrome, Ultrapycnometer 1000) under helium purge at pressure of 20 psi.

### 3.3.7 Impedance/Gain-Phase Analyzer

Dielectric properties of PVDF film and laminated PVDF film were measured by impedance/gain-phase analyzer (Hewlett Packard., model 4194A and Agilent., model E4980A) in parallel capacitance ( $C_p$ ) mode, with frequency from 1 kHz to 10 MHz at room temperature. The specimens were prepared by painting silver as electrode on both sides of the specimens. Before electroding, the major faces of specimens are polished parallel with silicon carbide powders size of 13 and 5  $\mu\text{m}$  in water slurry, respectively, and geometries are recorded. The dielectric constant of materials is calculate from the capacitance by using the following equation:

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

Where C is the capacitance (F),  $\varepsilon_0$  the free space dielectric constant value ( $8.85 \times 10^{-12}$  F/m), A the capacitor area ( $\text{m}^2$ ), and d the thickness of specimens.

### 3.3.8 Ferroelectric Measurement Test System

The polarization and electric field characteristics (Hysteresis loop) were measured by RT66A: standardized ferroelectric measurement test system. Voltage in the range of 1000-4000 Volts was applied to the specimens, which were immersed in silicone oil at room temperature to observe the hysteresis loops.

### 3.3.9 $d_{33}$ Meter

Stress piezoelectric coefficients ( $d_{33}$ ) of the polarized films were obtained from  $d_{33}$  meter (APC Int. Ltd., model 8000) operating at frequency of 1000 Hz and a time interval of 24 h after film polarization.

### 3.3.10 Compression Molding Machine

Laminated film samples were preformed by a compression press (Labtech, model LP 20).