CHAPTER III
EXPERIMENT

3.1 Materials

The poly(vinylidene fluoride) (PVDF) powder(#1008) material was kindly supported by Solvay (Thailand) Limited;. Azo-dicabonamide (blowing agent) was provied by Usaco (Thailand) Limited. The solvents used were *N,N*-Dimetyl acetamide (DMAc, 99.5%), *N,N*-Dimetyl formamide (DMF, 99.8%) were purchased from Lab Scan Co., Ltd. and Triethylphosphate (TEP, 98%) was obtained from Fluka Co., Ltd. All chemicals are used without further purification.

3.2 Equipments

- FTIR Spectrometer (Thermo Nicolet, Nexus 670)
- Scanning Electron Microscope (SEM) (JEOL, JSM-5200)
- X-ray Diffraction Microscope (XRD) (Rigaku, model Dmax 2002)
- Particle Size Analyzer (PSA) (Mastersizer, X)
- Thermogravimetric Analyzer, TGA (Perkin Elmer)
- Differential Scanning Calorimeter, DSC7 (Perkin Elmer)
- Impedance/Gain-Phase Analyzer (Hewlett Packard., model 4194A)
- RT66A (Ferroelectric Measurement Test System)
- d_{33} meter (APC Int. Ltd., model 8000)
- Ultrapycnometer 1000(Quantachrome version 2.4)
- Compression Molding Machine (Wabash, model V50H-18-CX)
- Universal Testing Machine (LLOYD LRX)
- Brabender Mixer W50
- Optical Microscope research stereo (SZH 10, OLYMPUS)

3.3 Experiment Procedure

3.3.1 PVDF Films Preparation

Poly(vinylidene fluoride) powders manufactured from Solvay Company (Belgium) (Solef 1008) are used. The fabrication of flat PVDF film is compression molding method which PVDF films are prepared by Wabash compression. From this method, PVDF powder is pre-heated at 180°C for 5 min, and then compressed it for 5 minutes under pressure 15 tons. The thickness of the prepared films ranged between 100-200 μm. The method was shown in Figure 3.1.

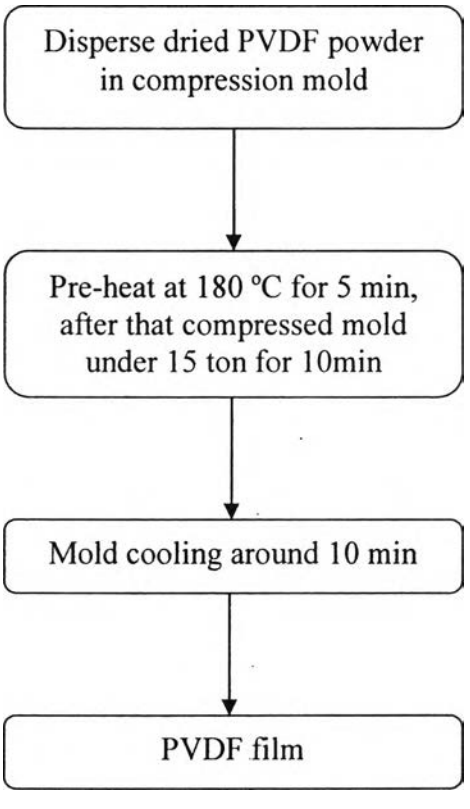


Figure 3.1 Fabrication procedures for PVDF films.

3.3.2 Porous PVDF Films Preparation (by phase inversion process)

Porous PVDF films are prepared by the isothermal immersion-precipitation method. First, PVDF powder was dried at 80°C for 24 hours in order to remove the amount of water and placed in desiccators prior to use. The preparation started by dissolving in solvent at 120°C. Polymer solutions are dispersed uniformly on a Teflon plate which thickness of casting layer was adjusted by a cast knife (ca. 100-150 μm thick). After that, immersed immediately into a distill water bath to induce phase separation at room T°. The formed membrane will wash in a series of nonsolvents and then dried under vacuum at 120°C for annealing the film that shown in Figure 3.2.

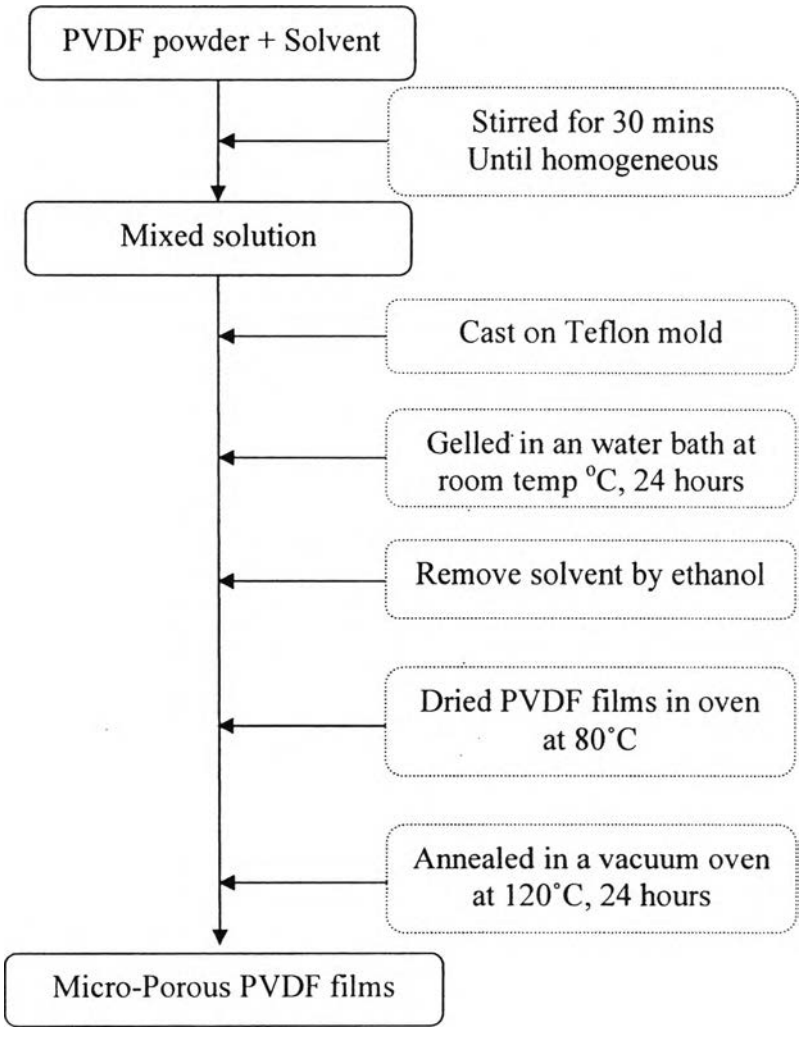


Figure 3.2 Fabrication procedures for micro-porous PVDF films.

3.3.3 Porous PVDF Film Preparation (by compression molding process)

The blowing agent as Azodicabonamide (AZDC) from Usaco (Thailand) Limited was used in this technique. The dried blowing agent was ground to powder and screened through a mesh #325. Then, AZDC was mixed with dried PVDF powder by brabender which rotor speed 50 rpm and temperature 190°C in 30 min or until torque graph in computer show the constant. Finally, a mixed powder was put on the mold and placed in compression molding machine, the temperature of which was pre-set at 200°C. After a 5 min holding period, the mould was cooled to room temperature.

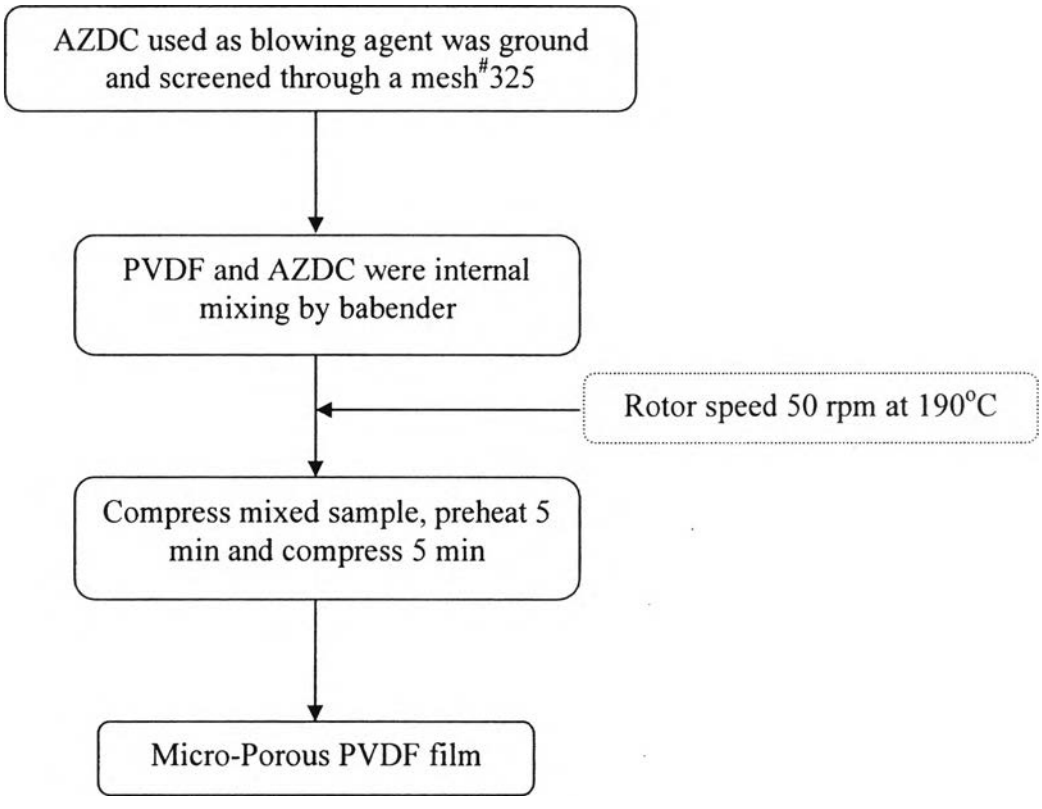


Figure 3.3 Fabrication procedures for micro-porous PVDF films by blowing agent.

3.3.4 Preparation for Dielectric and Piezoelectric Properties in Porous PVDF film

A uniaxial stretching (α to β transformation) typical stretch ratio 1:1, the sample is stretched up to one times its original length by Universal Testing Machine (LLOYD LRX) with Heater Chamber in order to prepare ellipsoidal shape of internal bubble. And then, subject the sample to large and enduring electric fields by thermal forming technique (for typical poling conditions the electric field is approximately 50 kV/mm at 90°C).

Equipment Setup

According to the study of bubbles shape between spherical and ellipsoidal, the temperature of stretching is significant which achieved during stretching at ~ 90°C. Thus, the construction of heater band is required in this research.

A. Heater band for stretching film

A schematic diagram of the heat chamber system can be classified into 2 sections for studying as follows in Figure 3.4.

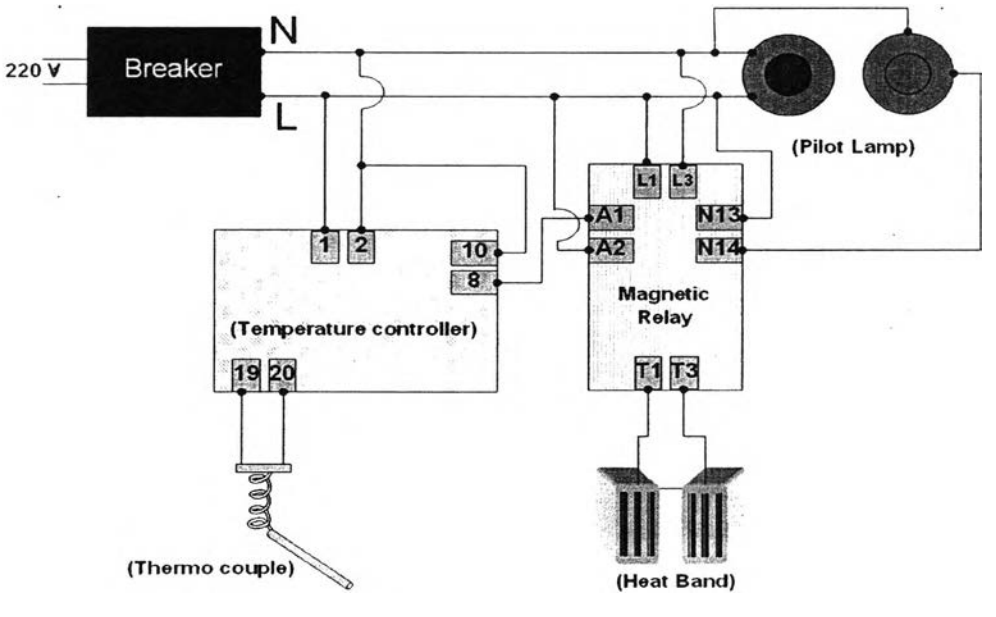
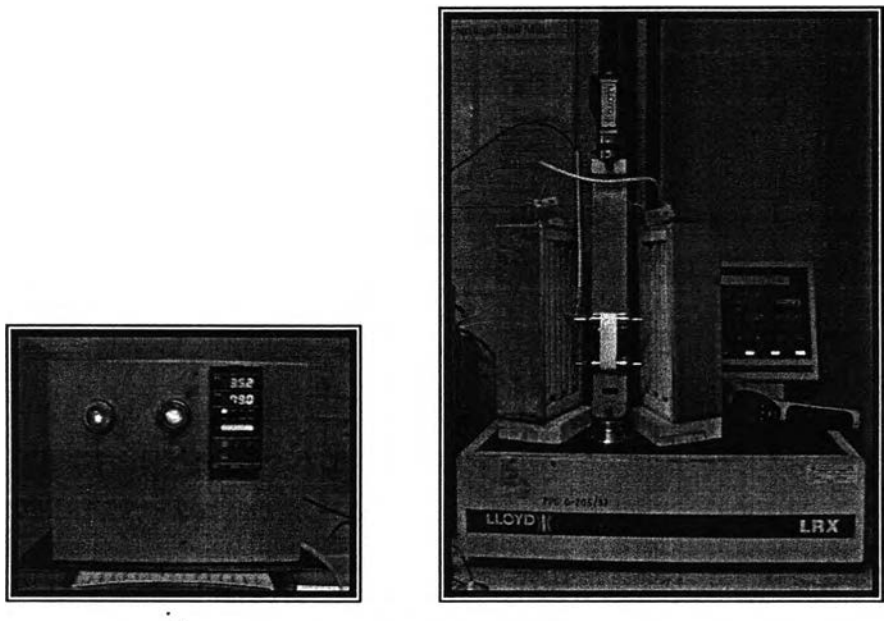


Figure 3.4 The schematic diagram of heater band.



(a) (b)

Figure 3.5 Heat chamber system consists of (a) temperature controller and (b) heater band section.

The temperature control system as show in Figure 3.5 (a) is digital type that can be used PID or on-off control, and suitable for K type of thermocouple which detect temperature. Figure 3.5 (b) shows the heater band that provides heat to PVDF film.

3.4 Characterization and Testing

3.4.1 Fourier Transformation Infared Spectroscopy (FTIR)

The Crystalline of porous 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 α and β phase the relative fraction of the β phase, $F(\beta)$, can be calculated by the following equation:

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{0.81A_\alpha + A_\beta}$$

Where X_α and X_β are the degree of crystallinity of α and β phases, A_α and A_β are the absorbances of α and β phases at 530 and 510 cm^{-1}, respectively.

3.4.2 X-ray Diffraction (XRD)

A crystal phase and structure of porous film PVDF are analyzed by X-ray diffraction (Rigaku, model Dmax 2002) with Ni-filtered CuKα radiation operate at 40 kV and 30 mA. The crystallinity of PVDF film is calculated by the following formula:

$$\text{Degree of crystallinity} = \frac{S_c}{S_c + S_a} \times 100\%$$

Where S_c and S_a are the sum of areas of the crystalline parts and amorphous parts. The β / α value could be obtained by calculating the ratio of the crystallinity of α to β phase.

3.4.3 Differential Scanning Calorimeter (DSC7)

Heating profiles of PVDF film and PVDF Porous film was performed by a differential scanning calorimeter 7, DSC 7 (Perkin Elmer) at a heating rate of 10°C/min. The samples are heated from 30°C to 300°C. Different scanning calorimetry (DSC) was used to determine the crystallization temperature for the dynamic phase diagram.

3.4.4 Thermogravimetric Analysis (TGA)

Thermal degradation was performed by a high resolution TG-DTA Pyris Diamond (Perkin Elmer). Samples are loaded on a the platinum pan heated from 30°C to 950°C with a heating rate of 10°C/min under N_2 flow.

3.4.5 Scanning Electron Microscope (SEM)

The structure and morphology on surface, cross-sections of porous PVDF films are observed by scanning electron microscopy (SEM). The cross section of porous PVDF films was freeze-fractured under liquid nitrogen. The porous PVDF film samples are gold sputtered and analyzed by using a scanning electron microscope (JEOL, model JSM 2590). The operating voltages were 15 kV.

3.4.6 Pycnometer

The apparent density of flat PVDF and porous PVDF film are measured by pycnometer (Quantachrome, Ultrapycnometer 1000) under helium purge at pressure of 17 psi.

3.4.7 Compression Molding Machine

PVDF film and PVDF porous film samples are preformed by a compression press (Wabash, model V50H-18-CX) with preheating 5 min, followed by compressing 5 min at a force of 15 kN. The operating temperatures of mould were maintained at 200°C.

3.4.8 Impedance/Gain-Phase Analyzer

Dielectric properties of PVDF film and porous PVDF film are measured by impedance/gain-phase analyzer (Hewlett Packard., model 4194A) in parallel capacitance (C_p) mode, with frequency from 1 kHz to 10 MHz at room temperature. The specimens are prepared by sputtering gold as electrode on both sides of the specimens. The dielectric constant of materials is calculated from the capacitance by using the following equation:

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

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

3.4.9 Ferroelectric Measurement Test System

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

3.4.10 d_{33} Meter

Stress piezoelectric coefficients (d_{33}) of the polarized films will be 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.

3.4.11 Porosity measurements

The appropriately measured PVDF membranes are immersed in i-butanol for 24 h and taken out to be weighed immediately after removing i-butanol on the surface. The porosity will be calculated according to the formula:

$$A_k = \frac{(W_2 - W_1)\rho_1}{\rho_1 W_2 + (\rho_2 - \rho_1)W_1} \times 100\%$$

Where W_1 is the initial membrane weight, W_2 is the immersed membrane weight, ρ_1 is the density of PVDF, and ρ_2 the density of i-butanol.

3.4.12 Brabender Mixer

Brabender Mixer W50 was used for internal mixing between PVDF powders and blowing agent before using compression molding. The rotor speeds were operated at 50 rpm. The processing temperatures were operated at 190°C.