CHAPTER III
EXPERIMENTAL

3.1 Materials

- High Density Polyethylene or HDPE (EL-Lene™ H377C) resin was provided by Thai Polyethylene Co., Ltd. (TPE).
- Polypropylene or PP (EL-PRO™ P600F) resin was provided by Thai Polyethylene Co., Ltd. (TPE).
- Polyvinyl chloride or PVC (PG740G2) powder was provided by TPC Paste Resin Co., Ltd.
- Azodicarbonamide or ACA (chemical blowing agent Microtech AC 505) was provided by Usaco (Thailand) Co., Ltd.
- Tetrahydrofuran or THF 99.5% purity was purchased from Carlo Erba Co., Ltd.
- *N,N*-dimethylactamide or DMAc 99.5% purity was purchased from Labscan Asia Co., Ltd.

All materials were used without further purification.

3.2 Equipment

- Internal Mixer (Brabender, PLASTOGRAPH) to mix polymer with blowing agent
- Compression Molding Machine (Wabash, model V50H-18-CX) to prepare dense and voided films
- Optical Microscope Research Stereo (SZH 10, OLYMPUS) to characterize morphology and dispersion of internal voids
- Field Emission Scanning Electron Microscope, FE-SEM (Hitachi, S-4800) to characterize morphology and dispersion of internal voids
- Fourier Transform Infrared Spectrometer, FTIR (Nicole/Nexus 670) to confirm the absence of blowing agent after compress polymer–ACA compounds

- Ultrapycnometer 1000 (Quantachrome version 2.4) to measure density of dense and voided films
- Density Kit (Sartorius, YDK01) to measure specific gravity of dense and voided films
- Differential Scanning Calorimeter, DSC7 (Perkin Elmer) to characterize crystallization temperature (T_c), glass transition temperature (T_g) and melting temperature (T_m)
- Thermogravimetric Analyzer, TGA (Perkin Elmer) to characterize decomposition temperature (T_d)
- Universal Testing Machine (LLOYD LRX) to stretch film and measure mechanical properties (tensile test)
- Universal Testing Machine (Instron/4206-006) to measure mechanical properties (flexural test)
- Electric Puncture Tester (Yasuda Seiki, model 175 YSS) to measure dielectric strength
- Impedance/ Gain-Phase Analyzer (Hewlett Packard., model 4194A) to measure dielectric constant and dielectric loss
- Ferroelectric Measurement Test System (RT66A) to measure ferroelectric properties
- d_{33} meter (APC Int. Ltd., model 8000) to measure piezoelectric coefficient

3.3 Methodology

3.3.1 Preparation of Dense Films

The dense HDPE and PP films were produced by a compression molding method.

3.3.1.1 Dense HDPE film

HDPE pellets was pre-heated at 135 °C for 8 minutes and compressed at 200 °C and load 15 tons for 10 minutes. The film was kept in the mold until it was cooled down to 50 °C.

3.3.1.2 Dense PP film

PP pellets was pre-heated at 170 °C for 8 minutes and compressed at 200 °C and load 15 tons for 10 minutes. The film was kept in the mold until it was cooled down to 50 °C.

3.3.1.3 Dense PVC film

PVC is an easily degraded material so the PVC films cannot be prepared by compression molding. Phase separation technique was used instead.

PVC powder (14 wt% PVC) was dissolved in THF and casted on the Teflon mold. The casted solution was left to solidify at room temperature for 24 hr and dried in vacuum oven at 48 °C for 24 hr to remove residual solvent and anneal film.

3.3.2 Preparation of Voided Films

The voided HDPE and PP films were processed by a compression molding method. The polymer–blowing agent compounds were blended with the Brabender mixer. The dried ACA was ground into powder and screened through a sieve (mesh #325) before using. ACA has decomposition temperature range 200 °C to 210 °C and gas volume is 215-225 ml/g.

3.3.2.1 Voided HDPE films

ACA and HDPE pellets were homogeneously blended with the Brabender mixer which set the rotor speed at 45 rpm and temperature at 145 °C. The temperature of molten compounds were 138.5 °C to 141 °C. Concentrations of 0.5 %, 1 %, 1.5 %, 2 %, and 2.5 % were used on the basis of the total weight of HDPE. Compounds were pre-heated and compressed at the same condition as dense HDPE film.

3.3.2.2 Voided PP films

ACA and PP pellets were homogeneously blended with the Brabender mixer which set the rotor speed at 45 rpm and temperature at 175 °C. The

temperature of molten compounds were 167.2 °C to 170.5 °C. Concentrations of 0.5 %, 1 %, 1.5 %, and 2 % were used on the basis of the total weight of PP. Compounds were pre-heated and compressed at the same condition as dense PP film.

3.3.2.3 Voided PVC film

Solvent cast of PVC films were obtained by casting a DMAc or THF solution of 8, 11, and 14 wt% PVC on the Teflon mold. The films were pre-evaporated for 5 minutes in air (25 °C ± 2 °C, 50 % RH ± 5 % RH) and then immersed in 25 °C distilled water bath for 24 hr. After that, the films were washed in the series of distilled water. To ensure that the residual solvent was removed out, these films were dried at 48 °C for 24 hr in vacuum oven. This condition will also be helpful to anneal the films to minimize the swelling of the films.

3.3.3 Preparation of Stretched Voided Films

The ellipsoidal voided films were obtained by stretching with Universal Testing Machine (LLOYD LRX) and heater chamber in Figure 3.1.

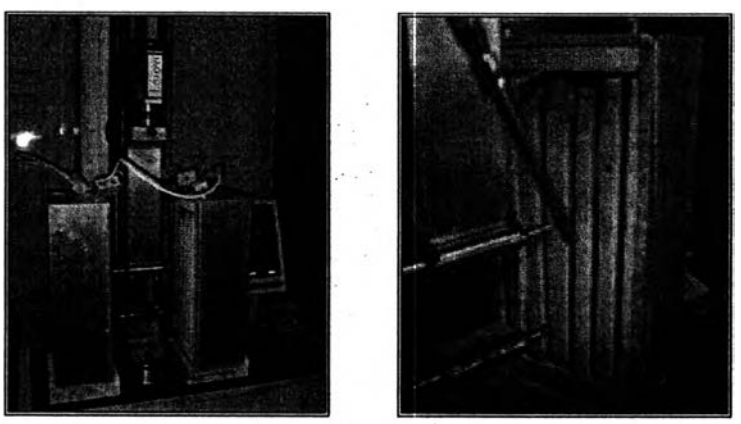

Figure 3.1 The heater band equipment for stretching voided films.

3.3.4 Characterizations

3.3.4.1 Morphology

The morphology and pore distribution of voided HDPE and PP films were performed using the Optical Microscope and the magnification of the images was 4X and the voided PVC films were performed using FE-SEM and the magnification of the images was 5000X.

3.3.4.2 Density and Porosity

Densities of dense and voided HDPE and PP films were measured by the Gas Pycnometer under helium purge at pressure of 20 psi. The average value of ten data was reported. Densities of dense and voided PVC films were measured by the density kit. The samples were weight in the air, then weight the samples in the deionized water. The specific gravity can be calculated from the equation shown below;

$$\rho = \frac{W(a) \cdot \rho(fl)}{W(a) - W(fl)}$$

Where ρ = specific gravity of the sample (g/mL)

W(a) = weight of the sample in air

W(fl) = weight of the sample in liquid

ρ(fl) = density of the liquid

The average value of five data was reported. Then, the porosities were calculated as:

$$\text{Porosity (\%)} = \left(1 - \frac{\rho_f}{\rho_m}\right) \text{x } 100\%$$

where ρ_m is the density of dense film and ρ_f is the density of voided film.

3.3.4.3 Crystallization Temperature, Glass Transition Temperature and Melting Temperature

Heating profiles of dense and voided films were performed by DSC7 at a heating rate of 10 °C/min. There are three steps for temperature profile.

Step 1: Heating 30 °C to 200 °C (To delete thermal history)

Step 2: Cooling 200 °C to 30 °C (To measure T_c of material)

Step 3: Heating 30 °C to 200 °C (To measure T_g or T_m of material)

3.3.4.4 Decomposition Temperature

Thermal decomposition was performed by TG-DTA. Samples were loaded in the platinum pan heated from 30 °C to 700 °C for HDPE and PP and heated from 30 °C to 850 °C for PVC with a heating rate of 10 °C/min under gas N_2 flow of 100 ml/min.

3.3.4.5 Mechanical Properties (Flexural test)

Flexural properties were evaluated as a function of blowing agent concentration using LLOYD with a 5 kN load cell. The samples were cut according to ASTM D790. A three-point bending fixture was used. The span of 80 mm, the span to depth ratio of 32/1, and the cross head speed of 4.1 mm/min were used. Temperature of 22 °C $\pm$ 2 °C and relative humidity of 48 % $\pm$ 4 % were controlled during measurement. From each experiment, Flexural strength and flexural modulus were obtained. Each test result was the average of 5 specimens.

3.3.4.6 Mechanical Properties (Tensile test)

Uniaxial tension mechanical properties were evaluated as a function of blowing agent concentration using LLOYD with a 500 N load cell. The samples were cut in a rectangular shape of 50 x 150 mm^2 (width x length). The gauge length of 50 mm and a crosshead speed of 50 mm/min was used. Temperature of 22 °C $\pm$ 2 °C and relative humidity of 48 % $\pm$ 4 % were controlled during measurement. From each experiment, results of Young's modulus, stress at break and percentage strain at break were obtained. Each test result was the average of 5 specimens.

3.3.4.7 Dielectric Strength

Dielectric strength was measured by the electric puncture tester. The samples in rectangular shape of 2.5x4 cm^2 (width x length) were tested. The electrode was spherical type and the short-time test was used. Temperature of 22 °C ± 2 °C and relative humidity of 48 % ± 4 % were controlled during measurement. The average value of 5 specimens was reported. In each case, the results are reported as the average value plus/minus one standard deviation.

3.3.4.8 Dielectric Constant and Dielectric Loss

Dielectric properties of dense and voided films were measured by the LCR meter with the frequency from 1 kHz to 1 MHz at various temperatures. The specimens were coated by 0.79 cm^2 of silver paint as electrode on both sides of the films before testing. Temperature of 22 °C ± 2 °C and relative humidity of 48 % ± 4 % were controlled during measurement.

3.3.4.9 Ferroelectric Properties

The correlation between polarization and electric field were measured by RT66A. Voltage in the range of 1000 volts to 4000 volts was applied to the specimens. The specimens were coated by 0.79 cm^2 of silver paint as electrode on both sides of the films before testing. Then samples were immersed in the silicone oil at room temperature during measuring. Temperature of 22 °C ± 2 °C and relative humidity of 48 % ± 4 % were controlled during measurement.

3.3.4.10 Piezoelectric Coefficient

Stress piezoelectric coefficients (d_{33}) of the polarized films were measured from d_{33} meter operating at the frequency of 1 kHz and a time interval of 24 hr after poling. The specimens were coated by 0.79 cm^2 of silver paint as electrode on both sides of the films before testing. Corona poling was carried out in atmosphere air at a relative humidity of 44 % to 52 %. Temperature of 22 °C ± 2 °C and relative humidity of 48 % ± 4 % were controlled during measurement.