

CHAPTER III EXPERIMENTAL

3.1 Materials

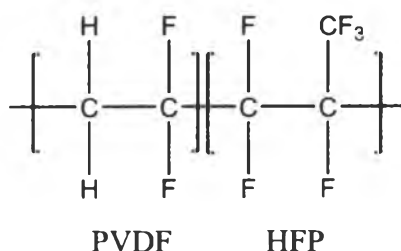


Figure 3.1 Chemical structure of PVDF-HFP.

Poly(vinylidene fluoride-co-Hexafluoropropylene) or PVDF-HFP with a melt flow rate of 7 g/10 min (5 kg at 230°C), Solef[®] 1010/1001 from Solvay was purchased from Prostar Chemicals Co., Ltd., Thailand.; Bagasse flour and Nata de coco were purchased from local food market; Hydrochloric acid (HCl) was purchased from RCI labscan Co.,Ltd.; Hydrogen peroxide (H₂O₂) was purchased from Chem-Supply Pty Ltd.; Sodium hydroxide (NaOH) (AR grade, 98%) were purchased from Merck Ltd.

3.2 Equipments

3.2.1 Co-rotating Twin Screw Extruder

LTE-20-40 twin screw extruder (Lab Tech) was used to prepare neat PVDF-HFP, PVDF-HFP/MCC composites, and PVDF-HFP/BC composite pellet. The operating temperatures were maintained at 150-160-165-170-175°C with screw speed of 30 rpm.

3.2.2 Film Casting Extruder

Neat PVDF-HFP, PVDF-HFP/MCC composites, and PVDF-HFP/BC composite film were prepared by a film casting extruder.

3.3 Methods

3.3.1 Microcrystalline Cellulose (MCC) preparation

Following the previous work of Thiangtham (2014), first, the bagasse flour was delignified using alkaline peroxide solution. The dried bagasse was treated with 10% (w/v) sodium hydroxide (NaOH) at 80°C for 4 hours to removed hemicellulose and lignin. The residue was washed with distilled water to remove NaOH. Then the delignified bagasse flour was bleached with 10% (v/v) hydrogen peroxide (H₂O₂) at 80°C for an hour until the wood became white. Second, the bleached wood flour was treated in 4M hydrochloric acid (HCl) at 80°C for an hour to hydrolyze to reach nano-sized. At the end of the extraction, the residue was continuously washed thoroughly with distilled water until neutral. The resulting cellulose was dried at 60°C for 2 days. Then, the dry cellulose was sieved to produce uniform powder with size less than 74 µm and defined as MCC.

3.3.2 Bacterial Cellulose (BC) Preparation (Ummartyotin *et al.*, 2012)

BC was extracted from the Nata de coco product. The Nata de coco was rinsed with distilled water to remove some excess sugar and blended using a laboratory blender to reduce the size and then was treated in 0.1M sodium hydroxide (NaOH) at 80°C for an hour to remove any remaining microorganisms, medium component and soluble polysaccharides. The purified bacterial cellulose (BC) was then thoroughly washed with distilled water until reaching neutral pH. After the extraction procedure, the BC was dried at 60 °C for 2 days. Then, the dry BC was sieved to produce uniform powder with size less than 74 µm.

3.3.3 PVDF-HFP/MCC and PVDF-HFP/BC Composite Film Preparation

All materials were generously pre-compounded and pelletized using a co-rotating twin-screw extruder (Lab tech LTE-20-40). The PVDF-HFP and MCC were dried at 60°C for 48 hours prior to processing. Pre-mixtures of PVDF-HFP with MCC with the dry weight ratio between PVDF-HFP and MCC of 1000:0, 99:1, 97:3 and 95:5 % by weight were blended in a laboratory blender to form uniform powder. The processing temperature, residence time and the screw speed were set at 150 - 175°C, 10 min and 30 rpm, respectively. The extruder barrel was equipped with two

atmospheric vents and vacuum ventilation in purpose to remove the vaporized water from the material.

Preparation of thin film was used the film casting extrusion. The PVDF-HFP and its composite pellets were dried at 60°C for 48 hours before film casting process. The temperatures of the extruder were set at 170-180°C. The screw speed for the samples was 65 rpm. The die temperature was fixed at 180°C. The chill roll was placed in 2 cm from the die and its temperature was kept at 20°C by temperature controller. The film was quenched by a chill roll to retain the resulting chain morphology (chain orientation) (Behzad *et al.*, 2007) and was transported to a pulling station using a nip roll. The speed of chill and nip rolls were controlled separately from the extruder using a dial and digital display. As reference, the neat PVDF-HFP film was also prepared in similar manner.

During the film blowing process, the polymer melt is biaxially stretched and in the following step the blown film is rapidly cooled down to room temperature to retain the resulting chain morphology (chain orientation).

For PVDF-HFP/BC composite film were also prepared in the same procedure as mentioned above.

3.4 Characterizations

Physical Properties

3.4.1 Scanning Electron Microscope (SEM)

SEM (a JOEL JSM-6301F scanning microscope) operating at an acceleration voltage 15kV was used to observe the morphology of MCC powder and BC powder.

3.4.2 Field emission scanning electron microscope (FE-SEM)

For the microstructural analysis of the PVDF-HFP film, PVDF-HFP/MCC composite films, the samples were previously frozen in liquid N₂, cryo-fractured and sputtered with platinum particles to obtained cross-sections. The obtained cross-sections were investigated by FESEM.

To studied dispersion morphology of MCC in the PVDF-HFP matrix, the samples were placed on carbon tape and sputter-coated with platinum particles to avoid charging.

3.4.3 Optical Microscopy

The dispersible morphology of MCC and BC at different contents in PVDF-HFP matrix was observed using optical microscopy (Leica, DM RXP). The thin sections of the composite films were used as samples.

Chemical Properties

3.4.4 Fourier Transform Infrared Spectrometer (FT-IR)

The crystalline of the neat PVDF-HFP, and its composites film were evaluated by using a Nicolet iS5 FT-IR spectrometer. All FT-IR absorption spectra were recorded in the 4000 to 650 cm^{-1} wave number region at a resolution of 8 cm^{-1} with 64 scans.

The vibration bands at 530 cm^{-1} (CF_2 bending), 615 and 763 cm^{-1} (CF_2 bending and skeletal bending) and 795 cm^{-1} (CF_2 rocking) refer to α -phase. The vibration bands at 509 cm^{-1} (CF_2 bending), and 840 cm^{-1} (CH_2 rocking) correspond to β -phase (Salmi *et al.*, 2004; Dahan *et al.*, 2012). Gregorio *et al.*, (1995) measured the degree crystallinity of α and β -phase, assuming the IR absorption follows Beer's law. The α -phase had a characteristic infrared absorption at 763 cm^{-1} , and they assumed that the 840 cm^{-1} absorption band is uniquely characteristic of the β -phase. Thus, for a system containing α and β phase, the relative fraction of the β phase was determined by comparing the absorbance of vibration band peaks of the samples at 840 and 763 cm^{-1} . Supposing that IR absorption follows the Lambert–Beer law, the A absorbance is given by

$$A = \log\left(\frac{I^0}{I}\right) = KCXL \quad (3.1)$$

Where L is the thickness of samples, C is the average total monomer concentration, I^0 and I are the incident and transmitted intensity radiations, respec-

tively, K is the absorption coefficient at the respective wave number, and X is the degree of crystallinity of each phase.

From the average crystalline densities of α (1.925 g/cm³) and β (1.973 g/cm³) phase, C value of 0.0305 mol/cm³ was determined. The absorption coefficients of $K_\alpha = 6.1 \times 10^4$ and $K_\beta = 7.7 \times 10^4$ cm²/mol at 763 and 840 cm⁻¹, feature of α and β -phases, the fraction of β -phase, $F(\beta)$, can be calculated using the following equation:

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(X_\alpha + X_\beta)A_\alpha + A_\beta} = \frac{A_\beta}{(1.26)A_\alpha + A_\beta} \quad (3.2)$$

Where X_α and X_β are the degree of crystallinity of α and β -phases, A_α and A_β are the absorbance at 763 and 840 cm⁻¹, respectively.

3.4.5 X-ray Diffraction (XRD)

Crystal phase and structure of the MCC, BC powders, PVDF-HFP, and its composites film were analyzed by using a XRD (Rigaku, model Dmax 2002) with Ni-filtered CuK α radiation operated at 40 kV and 30 mA. The samples were scanned at 2θ angles from 10-80° with a scanning speed of 5°C/min. The crystallinities of the MCC and BC were calculated with the Segel's method;

$$\text{Crystallinity}(\%) = \frac{I_{22.7} - I_{18.0}}{I_{22.7}} \times 100 \quad (3.3)$$

Where $I_{22.7}$ is the intensity of the peak at $2\theta = 22.7^\circ$ and corresponds to crystalline and amorphous cellulose, and $I_{18.0}$ is the intensity of the peak at $2\theta = 18.0^\circ$ which correspond to amorphous cellulose only.

For PVDF-HFP, β phase will show the peak at $2\theta = 20.4^\circ$ and 23.65° that are corresponding to the sum of diffraction in (200) and (110) planes, also the exhibition of peak at $2\theta = 17.7^\circ$, 18.4° , and 19.9° refers to the diffraction in (100), (020) and (201) planes respectively of α phase. Furthermore, peaks at 14.8° , 16.2° , and 22.6° indicate the presence of cellulose crystal structure (Hartshorne *et al.*, 2004).

Thermal Properties

3.4.6 Differential Scanning Calorimeter (DSC)

Mettler[®] Toledo DSC 822^e was used to observe the phase transition and thermal behavior such as melting temperature (T_m), crystallization temperature (T_c), and specific heat capacity. An empty aluminum pan was used as a reference. Prior to DSC runs, the temperature and heat flow were calibrated using indium standards. Each sample (5-10 mg) was heat at a heating rate of 10 °C/min under nitrogen atmosphere. The condition comprised three steps (heat-cool-heat). First, the temperature was set from 30°C to 190°C to heat the sample for removing thermal history. Second, the temperature was cooled down to 30°C. Finally, the samples were subsequently heated to 190°C once more for corresponding melting behavior investigations. All of three steps were run under nitrogen atmosphere.

The degree of crystallinity was determined as the ratio between ΔH_m and ΔH_m^0 , as equation 3.1.

$$\% \text{ crystallinity } (X_c) = \frac{\Delta H_m}{\Delta H_m^0 \times \phi} \times 100\% \quad (3.4)$$

Where ΔH_m is the melting enthalpy of the material under study, ΔH_m^0 is the standard enthalpy of fusion of 100% crystalline (for PVDF-HFP, ΔH_m^0 is 104.7 J/g) and ϕ is the mass ratio of PVDF-HFP in the composite (Hwangb *et al.*, 2012).

3.4.7 Thermalgravimetric Analysis (TGA)

TGA (Perkin-Elmer Pyris Diamond TG/DTA instrument) was used to observe onset degradation temperature (T_d) and %weight loss. The samples were analyzed at the temperature in range of 30-800°C at a heating rate of 10 °C/min and nitrogen flow of 50 ml/min.

3.4.8 Dynamic Mechanical Analysis (DMA)

DMA can measure stiffness and damping which reported as modulus and $\tan \delta$, respectively. In this research, DMA (Gabo Eplexor[®] 100N) was used to determine phase behavior of the blends like Tg. The temperature scan started from 80 to 150°C at frequency of 1 Hz and heating rate 2°C/min under tensile mode.

Electrical Properties

3.4.9 Dielectric measurement

To studies the frequency dependence of the dielectric constant and dissipation factor of the film, dielectric properties were investigated at 20°C in 2 region frequency range; at low frequency (1 kHz to 1MHz) using the LCR meter and high frequency (10 MHz to 1 GHz) using the impedance/gain-phase analyzer (Agilent, model E4991A).

Additional, to understand the temperature dependence of the dielectric constant and dissipation factor of the film, dielectric properties were measured at 10 MHz, 100 MHz, and 1 GHz at temperature range of -50 to 130 °C using the impedance/gain-phase analyzer (Agilent, model E4991A).

The dielectric constant of materials was calculated from the capacitance by using equation 3.3.

$$\epsilon = \frac{Cd}{\epsilon_0 A} \quad (3.5)$$

Where C is the capacitance (F), ϵ_0 is the free space dielectric constant value ($8.85 \times 10^{-12} \text{ F.m}^{-1}$), A is the surface area of the samples (m^2), and d is the sample thickness.

3.4.10 Piezoelectric measurement

Piezoelectric property was describes from the relationship between dielectric constant and Piezoelectric coefficient (d_{ij}) via equation 3.6.

$$d_{ij} = \epsilon_{ii} \epsilon_0 g_{ij} \quad (3.6)$$

Where d_{ij} is stress piezoelectric coefficient, ϵ_{ii} is the dielectric constant of the material, ϵ_0 is the free space dielectric constant value ($8.85 \times 10^{-12} \text{ F.m}^{-1}$), and g_{ij} is piezoelectric voltage coefficient. This equation shows that the dielectric property is a basic property for piezoelectric materials.

3.4.11 Mixture of Dielectrics

Most materials are in homogeneous and dielectric properties will be determined by volume fracture and distribution of different dielectric phase. To better understand the nature of the dielectric response of the composite material with increasing MCC content, several theoretical models were employed. The first model developed to predict the dielectric behavior of the composites was proposed by Maxwell in 1904; this model is still widely used. In this model, the dielectric response of the composite is given by:

$$\epsilon_T = \frac{V_{f1}\epsilon_1 \left(\frac{2}{3} + \frac{\epsilon_2}{3\epsilon_1} \right) + V_{f2}\epsilon_2}{V_{f1} \left(\frac{2}{3} + \frac{\epsilon_2}{3\epsilon_1} \right) + V_{f2}} \quad (3.7)$$

Where ϵ_T is the dielectric constant of the composite, ϵ_1 is the dielectric constant of the polymer, ϵ_2 is the dielectric constant of the filler, and V_{f1} and V_{f2} are the volume fractions of the polymer and filler, respectively.

And the second rule is Log mixing rule which developed to predict the dielectric behavior of the composites that contained spherical particle filler;

$$\epsilon_T = \epsilon_1^{V_{f1}} \cdot \epsilon_2^{V_{f2}} \quad (3.8)$$

Where ϵ_T is the dielectric constant of the composite, ϵ_1 is the dielectric constant of the polymer, ϵ_2 is the dielectric constant of the filler, and V_{f1} and V_{f2} are the volume fractions of the polymer and filler, respectively.

Mechanical Properties

3.4.12 Universal Testing Machine (UTM)

The mechanical tests were carried out by using Lloyd Instruments. The tensile specimens were prepared according to the ASTM D638 standard (10 cm x 1 cm with >300 μm of thickness) with the crosshead speed of 50 mm/min and 2500 N of load cell. The initial distance between grips was 50 mm. At least 10 specimens were tested per sample to obtain a statistical average.

Optical Properties

3.4.13 UV/Visible spectrophotometer

The percentage of transmittance of the PVDF-HFP and its composites film was observed by using a UV/visible spectrophotometer (Avaspec-2048) at room temperature, 400-900 nm wavelength, and 2.0 nm slit width with middle speed scan rate. A base line was calibrated using a polytetrafluoroethylene (PTFE) reference cell.

Thermal Stability

3.4.14 Thermal Shrinkage (ASTM D 2732)

Thermal shrinkage at high temperature causes the internal short circuit, measuring the thermal shrinkage is very important to evaluate the thermal stability of the touch sensor. The sample areas were measured before and after thermal treatment at different temperatures (80, 90, 100, 110, and 120°C) for 30 min and for different times (30, 60, 90, and 120 min) at 110°C to analyze the thermal shrinkage properties. Immerse the specimen in the bath then remove the specimen from the bath and quickly immerse in a liquid medium at room temperature. After 5 seconds, remove the specimen from the cooling medium and measure the linear dimensions of the specimen in both the machine and transverse directions.

The percent shrinkage for each direction was calculated using equation 3.9. Where L_i and L_f are the initial and final length of each side.

$$\text{Shrinkage (\%)} = \frac{L_i - L_f}{L_i} \times 100 \quad (3.9)$$