CHAPTER III
EXPERIMENTAL

3.1 Materials

Nata de coco was purchased from local food market. Poly(vinylidene fluoride) (PVDF) (SOLEF1008) was kindly supported by Solvay (Thailand) Co., Ltd. N,N-dimethylformamide (DMF) (AR grade, 99.8%) and sodium hydroxide (NaOH) (AR grade, 98%) were purchased from RCI labscan Co., Ltd. and Merck Ltd., respectively. 0.01 M silver nitrate solution ($AgNO_3$) and 0.5 M sodium borohydride solution ($NaBH_4$) were purchased from Sigma-Aldrich Co., Ltd.

3.2 Experimental Procedures

3.2.1 Bacterial Cellulose (BC) Preparation (Maneerung *et al.*, 2008)

Figure 3.1 shows the BC preparation. Nata de coco gel was firstly washed with water to remove some excess sugar. After that the washed nata de coco gel was grinded and treated with 0.1 M NaOH at 80 °C for 1 h to obtain the BC pellicles. The BC pellicles were then washed with hot deionized water until neutral pH is reached. The BC pellicles were dispersed in deionized water and kept in bottle. Density of BC pellicles would be determined after freeze-drying.

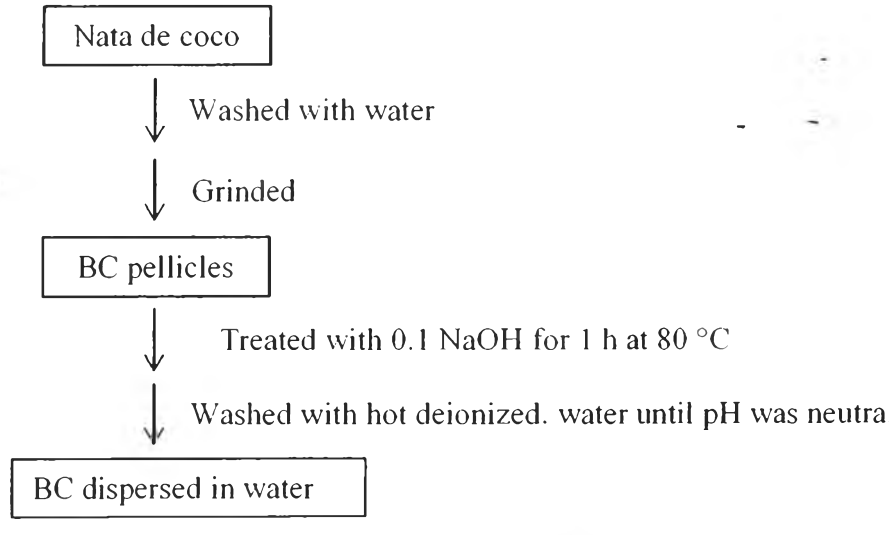

Figure 3.1 BC preparation.

3.2.2 BC/PVDF Blend Films Preparation

BC pellicles were rinsed with DMF solution to remove all water content. Then BC pellicles dispersed in DMF solution were obtained. PVDF pellets were dissolved in DMF solution to obtain 10 %wt/v PVDF solution. The obtained solution was further incorporated with BC dispersed in DMF solution with the percentage weight ratio (BC:PVDF) of 0:100, 2.5:97.5, 5:95, 10:90 and 15:85. Then the mixture of BC/PVDF solution was taken into the ultrasonic bath to allow well dispersion for 1 h. Then, the mixture solution was further dropped on clean glass substrates. After that, they were heated in vacuum oven at 80 °C for 3 days, the casted blend films were obtained. Finally, the casted film were performed by a compression press (Labtech, model LP20) with preheating for 20 min, followed by compressing for 15 min at 10 kN. The operating temperature of mould was maintained at 200 °C.

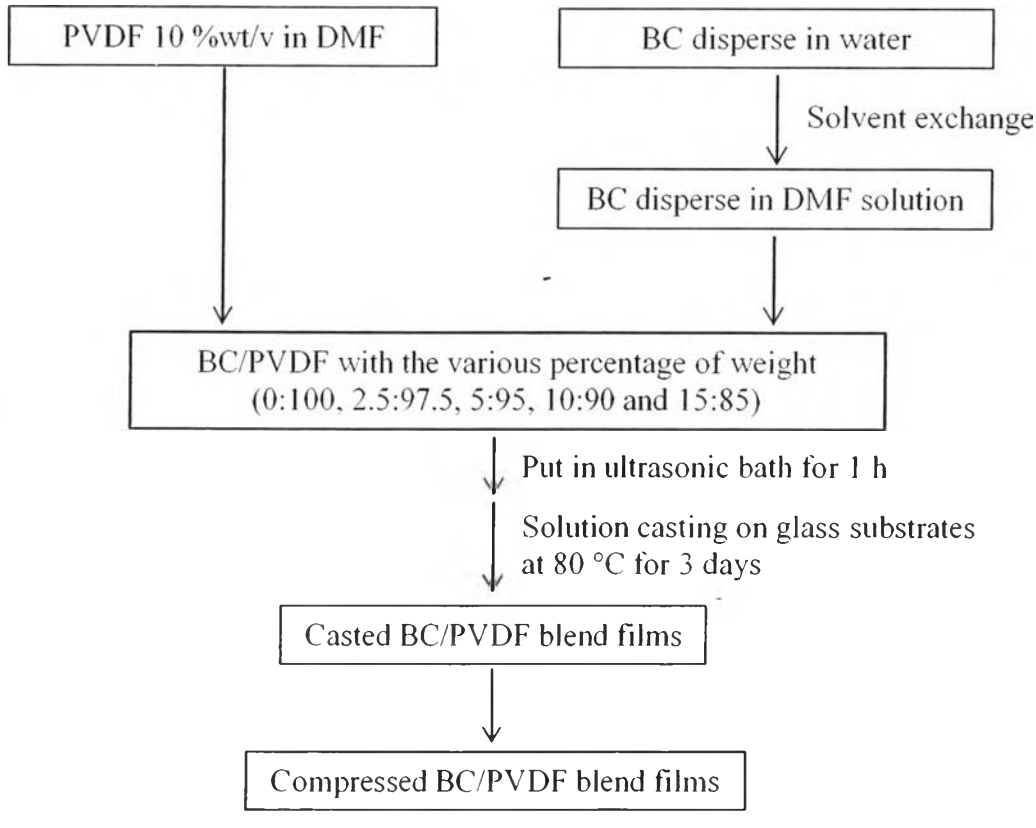

Figure 3.2 BC/PVDF blend films preparation.

3.2.3 Impregnation of Silver Nanoparticles (AgNP) into Bacterial Cellulose (Thawatchai et al., 2007)

As shown in figure 3.3, AgNP were impregnated into BC fiber by immersing the BC pellicles in 0.01 M $AgNO_3$ solution for 1 h to obtain 5 wt%, 10 wt% and 20 wt% of AgNP in BC. Then the silver ion-saturated BC pellicles were reduced with 0.01 M $NaBH_4$ solution for 10 min and rinsed with a large amount of deionized water for 30 min to remove the excess chemical. The obtained sample was dispersed in water and kept in bottle.

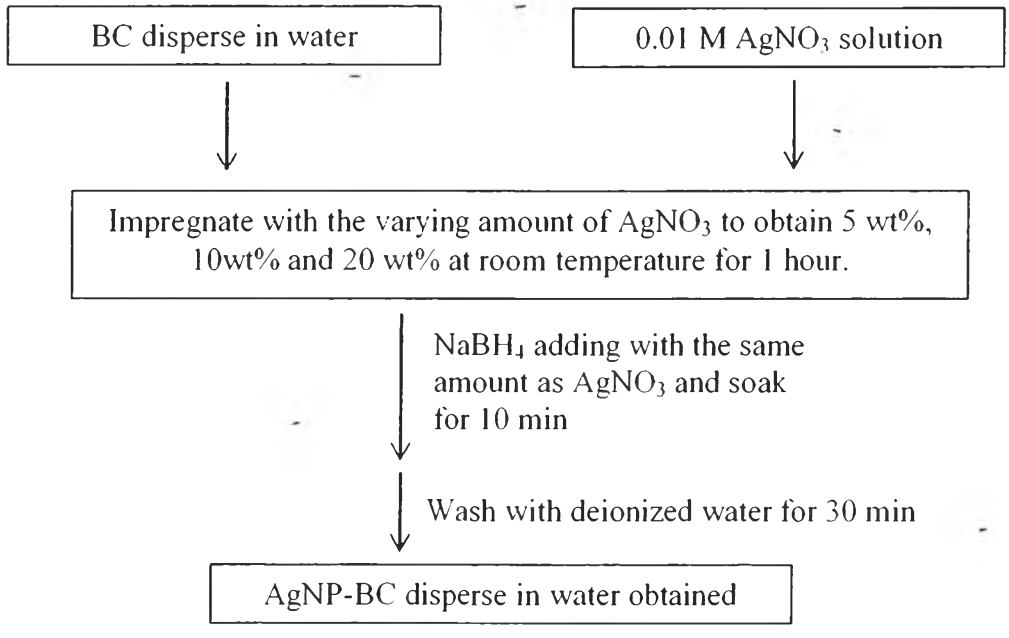

Figure 3.3 Impregnation of AgNP into BC.

3.2.4 Silver Nanoparticles in Bacterial Cellulose/Poly(Vinylidene Fluoride) Nanocomposite Films Preparation

The nanocomposite films were prepared as follow; AgNP dispersed in BC slurry was rinsed with DMF to remove all water content. Then, AgNP/BC dispersed in DMF was obtained. PVDF solution was mixed with AgNP/BC dispersed in DMF solution with the suitable composition ratio between BC and PVDF with 5, 10 and 20 wt% of AgNP in BC. Then the mixture solution was taken into the ultrasonic bath to obtain well dispersion for 1 h. The mixture solution was further dropped on clean glass substrates. After they were heated in vacuum oven at 80 °C

for 3 days, the casted nanocomposite films were obtained. Finally, the casted film were performed by a compression press (Labtech, model LP20) with preheating for 20 min, followed by compressing for 15 min at 10 kN. The operating temperature of mould was maintained at 200 °C.

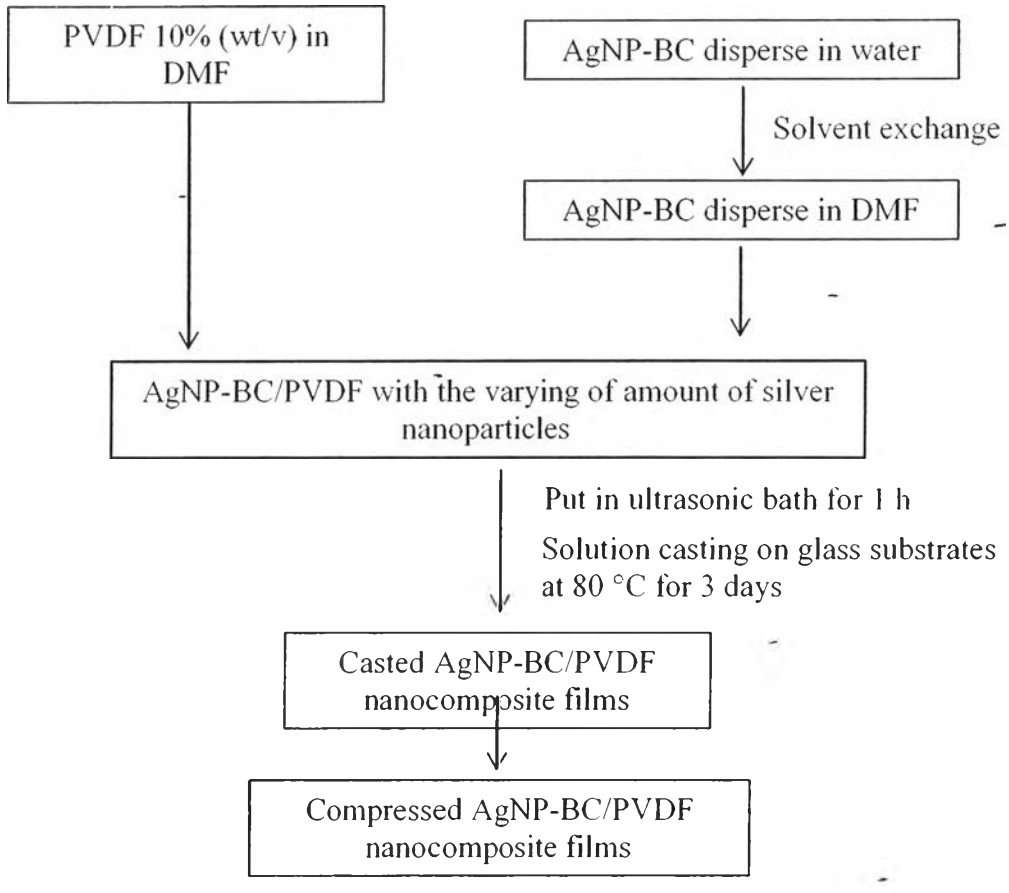

Figure 3.4 AgNP in BC/PVDF nanocomposite films preparation.

3.3 Characterizations

3.3.1 Scanning Electron Microscopy with Energy Dissipation Spectroscopy (SEM-EDS)

The morphology of BC, its blend films and its nanocomposite films can be investigated by SEM (TM3000). It operated at 15 kV. Cross-section samples were prepared. The cryo-fracture films were obtained by soaking the samples in liquid nitrogen for 5 min, then break the samples immediately at room temperature.

The prepare samples were sputtered with platinum for 150 s. EDS was also provided to investigate the presence of silver nanoparticles.

3.3.2 Transmittance Electron Microscopy (TEM)

The size, shape, and diameter of network fiber of BC and AgNP were observed by using a JEOL 2100. The solution samples were suspended in dispersing medium and dropped on a molybdenum grid and it was consequently dried at room temperature for 48 h. The acceleration voltage of electron beam was 1000 keV and images were captured under a magnification of 50,000.

3.3.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The crystalline of PVDF, blend films, and nanocomposite films were evaluated by using an a Bruker FT-IR spectrometer, model Vector 3.0 with Attenuated total reflectance FT-IR mode. The measurement was in absorbance mode with 64 scans per resolution. Thus, for a system containing α and β phase, the relative fraction of the β phase, F(β), will be calculated by the below equation:

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{1.26A_\alpha + A_\beta} \qquad (3.1)$$

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 765 and 840 cm^{-1}, respectively.

3.3.4 X-ray Diffraction Microscopy (XRD)

Crystal phase and structure of PVDF films were analyzed by using a Rigaku, model Dmax 2002, XRD with Ni-filtered CuKα radiation operated at 40 kV and 30 mA. The samples were scanned at 2θ ranging from 10° to 80° with a scanning speed of 5 °C/min.

For PVDF, β phase exhibit peaks at 20.4° and 36.7° that are corresponding to the sum of diffraction in (200) and (110) planes, but peaks at 17.7°, 18.6°, and 27° corresponds to the diffraction in (100), (020), and (201) planes, respectively, of α phase.

In addition, there are other peaks of 38.1°, 44.3°, 64.4°, and 78.0° refer to the diffraction plane of AgNP and the intensity depends on the amount of AgNP. Furthermore, peaks at 14.8°, 16.2°, and 22.6° indicate the presence of cellulose crystal structure.

3.3.5 Differential Scanning Calorimetry (DSC)

Heating profiles of PVDF films, BC/PVDF blends and BC/PVDF with silver nanoparticles nanocomposites films were performed by a differential scanning calorimeter 7, DSC 7 (Perkin Elmer) with a heating rate of 10 °C/min. Ten milligrams of samples were heated in aluminium pan from 50 °C to 200 °C. Differential scanning calorimetry, DSC is used to determine the crystallization temperature (T_c) and crystalline melting temperature (T_m) for the dynamic phase diagram. The degree of crystallinity will be measured as the ratio between ΔH_m or ΔH_c and ΔH_m^0, as below equation.

$$\% \text{ crystallinity } (X_C) = \frac{\Delta H_m, \Delta H_c}{\Delta H_m^o, \Delta H_c^o (1-\alpha)} \times 100\% \qquad (3.2)$$

where ΔH_m is the melting enthalpy of the material under study, ΔH_c is the crystallization enthalpy of the material under study and ΔH_m^0 is the melting enthalpy of totally crystalline material (100% crystalline), ΔH_m^0 for PVDF = 92.4 J/g , ΔH_c^0 is the crystallization enthalpy of totally crystalline material (100% crystalline), ΔH_c^0 for PVDF = 90.2 , and α is fiber weight content.

3.3.6 Thermal Gravimetric Analysis (TGA)

Thermal stability and degradation behavior of the films were studied by using thernogravimetric and differential thermal analyzer (TG-DTA) Pyris Diamond (Perkin Elmer). Ten milligrams of samples were loaded on the alumina pan and heated from 50 °C to 700 °C with a heating rate of 10 °C/min under N_2.

3.3.7 Tensile Properties Measurement

The tensile properties of the blend films were investigated by universal testing machine (Lloyd) with 2500 N of load cell. The tensile testing was followed the ASTM D882. Gauge length was fixed at 5 cm with the speed test at 50 mm/min. Samples were prepared into 10 cm x 1 cm with >300 μm of thickness.

3.3.8 UV/Visible Spectrophotometry (UV/Vis)

The transmission of films was collected by UV/visible spectrophotometer, UV/Vis (Shimadzu Scientific Instrument, model 2550) in the range of wavelength from 400 nm to 750 nm. Films were prepared into 1.5 cm x 3 cm with >300 μm of thickness.

3.3.9 Dynamic Mechanical Analysis (DMA)

DMA measurement was carried out with spectrometer DMA GABO EPLEXOR 100 N in tension mode. The samples were thin rectangular strip with a dimension of 50 mm x 10 mm x 0.4 mm and oscillated at 1 Hz. The samples were heated with a heating rate of 2 °C/min over the temperature ranging from -80 °C to 150 °C.

3.3.10 Dielectric Measurement

Dielectric properties of PVDF film, BC/PVDF blend films and AgNP-BC/PVDF nanocomposite films were measured by impedance/gain-phase analyzer (Agilent., model E4991A) with 10 MHz to 1 GHz and -50 °C to 150 °C to observe the dielectric behavior of materials. The samples were prepared by sputtering with 1 cm diameter circular shape platinum as electrode on both sides. The dielectric constant of materials was calculated from the capacitance by using below equation:

$$\varepsilon = \frac{Cd}{\varepsilon_0 A} \tag{3.3}$$

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