

CHAPTER III EXPERIMENTAL

3.1 Materials

Nata de coco was purchased from local food factory as a food grade. PVDF (J100) was supplied by Asambly Chemicals Company. N,N-dimethylformamide (DMF) and sodium hydroxide (NaOH) were purchased from RCI Labscan Co.,Ltd. and Merck Ltd., respectively. Carboxylic treated multi-walled carbon nanotube (>95% of carbon nanotube content) was purchased from Chengdu Organic Chemicals Company, Chinese Academy of Sciences, People Republic of China. The average diameter and length are less than 10 nm and 30 μm as technical data sheet.

3.2 Experimental Procedures

3.2.1 Extraction and Purification of Bacterial Cellulose

Bacterial cellulose (BC) were extracted from nata de coco product. The nata de coco gel were firstly rinsed with distilled water and blended using a laboratory blender. Then treated with 0.1 M NaOH at 80°C for 20 min to remove any remaining microorganisms, medium component and soluble polysaccharides. The purified bacterial cellulose will be then thoroughly washed with distilled water until reach the neutral pH as shown in Figure 3.1.

3.2.2 Preparation of Bacterial Cellulose Suspension in DMF

BC suspended in DMF as a disperse medium under stirring. Water was removed from the mixture by evaporation at 80°C for 2 hours. The homogeneous suspended BC in DMF was obtained.

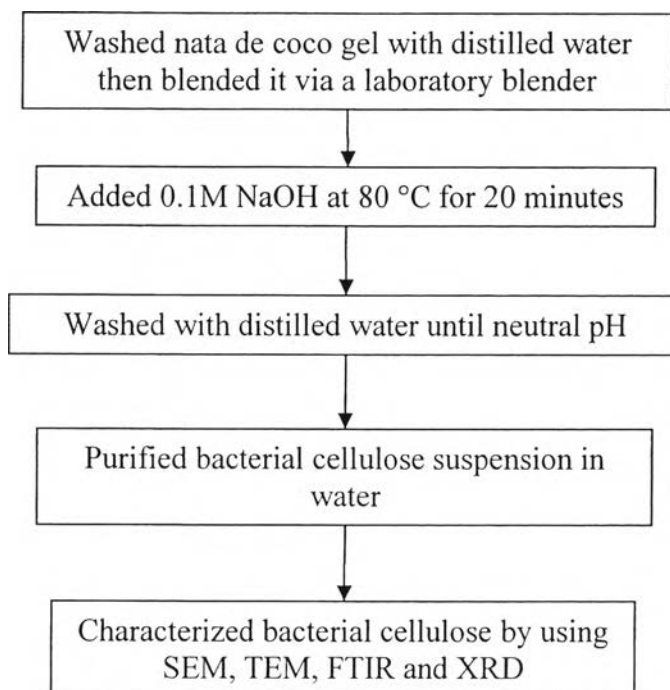


Figure. 3.1 Bacterial cellulose extraction and purification from nata de coco.

3.2.3 Fabrication of PVDF/BC Blend Films

The blend of PVDF/BC films were fabricated by two steps of solvent-casted and compression techniques. Firstly, the nanocomposite sheet were prepared by solvent casting technique. DMF was used as a polar solvent to dissolve PVDF at 60°C and stirred until got homogeneous solution. Then, PVDF and BC were mixed together at the desired weigh ratio 97.5/2.5, 95/5, 90/10, 80/20 and 60/40, respectively. The mixtures were stirred at 60°C for 30 minutes to obtain good distribution of BC in PVDF solutuion then poured on Petri dish glass. The solvent was vaporized in an oven at 80°C for 48 hours to remove all remaining solvent, the PVDF/BC nanocomposite films were obtained. Then, compression technique was used to make a dense sheet. The casted nanocomposites were cut into pellets, heat at 180°C for 20 minutes to obtain polymer in molten state. Followed by hot-press under 10 tons for 5 minutes, the thickness of composite films were about 1mm.

For MCNT addition, MCNT were dispersed in DMF using an ultrasonic probe for 30 minutes then filled in the mixture of PVDF/BC at different phr loading. The followed steps are as same as mention above.

3.3 Experiment

3.3.1 Fourier Transform Infrared (FTIR)

FTIR was performed on using a Thermo Nicolet, model NEXUS 670. The absorption peak was recorded over wavenumbers region of 4000-400 cm^{-1} by taking 64 scans with a resolution of 4 cm^{-1} using standard KBr tablet samples. To prevent humidity effect, samples and KBr were dried in an oven at 60°C. The fraction of β phase, $F(\beta)$, of the samples can be calculated using the followed equation;

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

Where A_{α} and A_{β} are absorbance in FTIR spectrum corresponding to at 763 and 840 cm^{-1} , respectively.

3.3.2 Scanning Electron Microscope (SEM)

The morphological properties of bacterial cellulose and its nanocomposite can be investigated by field emission scanning electron microscope (Hitachi, S-4800). It operated at acceleration voltage of 2 kV. Prior to investigation, the samples were stored in desiccators for humidity prevention. Then, each sample was sputtered with a thin layer of silver before analysis to prevent surface charged.

3.3.3 Transition Electron Microscope (TEM)

The diameter of network fiber of bacterial cellulose was observed by TEM, using a Hitachi H-7000. The samples were suspended in dispersing medium and dropped on a molybdenum grid and it was consequently dried at room temperature for 48 hours. The acceleration voltage of electron beam was set at 1000 keV and image was captured under a magnification of 50kx.

3.3.4 X-ray Diffraction (XRD)

Diffraction patterns of BC, neat PVDF and PVDF nanocomposites were obtained using a Bruker AXS Diffractometer D8 with Ni-filtered $\text{CuK}\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation operated at voltage of 40 kV and current of 30 mA. The samples were scanned at 2θ ranging from 10° to 50° with scanning speed 2°/min. The crystallinity index (CrI) of purified bacterial cellulose was calculated as followed equation 3.2:

$$\text{CrI} = \frac{I_{002} - I_{am}}{I_{002}} \quad (3.2)$$

Where I_{002} is the maximum intensity of peak at about $2\theta = 22.5$ and I_{am} is the intensity of amorphous peak at about $2\theta = 18$. (Adnan *et.al*, 2012)

The crystalline size of BC was calculated using Scherrer equation 3.3 as followed:

$$D_{hkl} = \frac{K\lambda}{\beta_0 \cos\theta} \quad (3.3)$$

Where D_{hkl} is crystallite size at diffraction plane hkl . β_0 is half the maximum intensity of broadening reflection in radian. λ is the x-ray wavelength (1.54056 Å). K is 0.94 and θ is the Bragg angle of diffracted rays.

3.3.5 Thermogravimetric Analysis (TGA)

The thermal stability of bacterial cellulose, neat PVDF and their nanocomposite were investigated by TGA (Perkin Elmers) as observed from degradation temperature. Each samples (5-7 mg) were heated with the heating rate of 10 °C/min with nitrogen atmosphere from 30°C to 900°C. The TGA balance flow meter was set at 30 psi of N₂.

3.3.6 Differential Scanning Calorimeter (DSC)

The glass transition temperature and melting temperature of neat PVDF and blend films were performed by DSC7 (Perkin Elmer) at a constant heating rate of 10°/min. The samples were heat-cool-heat to delete thermal histories from -50°C to 200°C. The crystallinity of nanocomposite (X_c) was calculated by equation 3.4:

$$X_c = \frac{\Delta H_m}{\Delta H_o(1-\alpha)} \quad (3.4)$$

Where α is fiber weight content, ΔH_o is the melt enthalpy for 100% crystalline PVDF (102.7 J/g).

3.3.7 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis measurement were carried out with spectrometer DMA GABO EPLEXOR 100N in tension mode. The samples were thin rectangular strip with a dimension about 40 mm × 10 mm × 0.5 mm and oscillated at frequency of 1 Hz. The specimens were heated at a heating rate of 2°C/min over the temperature ranging from 80°C to 150°C.

3.3.8 Network analyzer

Network analyzer (Agilent E4991A integrated with probe Agilent 16453A) was used to observed the dielectric behavior of materials at frequency 10 MHz -1 GHz and various temperature in a range of -50-100°C. Both sides of sample films were coated with silver paint at specific area of 0.785 cm² as an electrode.

3.3.9 d₃₃ Meter

The in-plane piezoelectric coefficient (d₃₃) of polarized samples were measured by d₃₃ meter (APC Int. Ltd., model 8000) operating at frequency 1000 Hz and room temperature. Before piezoelectric

3.3.10 Ferroelectric Analyzer

The ferroelectric behavior of the composite films were studied using the correlation between polarization (μC/cm²) and electric field (kV/cm). This test was measured by RT66A. The specimen were coated by silver paint as an electrode on both sides of sample at specific area of 0.785 cm². The films were immersed to silicone oil at room temperature to observed P-E hysteresis loops.

3.3.11 Compression Molding Mechine

The neat PVDF and PVDF composite films were prepared by a compression molding (Labtech) at 190°C under pressure of 1000 psi.