



## CHAPTER V

### PROTON CONDUCTIVITY IMPROVEMENT BY PVDF/PAN-ANTIMONY MODIFIED TITANIUM DIOXIDE (Sb-TiO<sub>2</sub>)

#### 5.1 Abstract

Solvent casting was used for preparing PVDF/PAN-5 mol% Sb-TiO<sub>2</sub> composite film. By blending polyvinylidene fluoride (PVDF) with polyacrylonitrile (PAN) in the weight ratio of 9:1 (PVDF: PAN), the film was expected to enhance the hydrophilicity. The composite films of 10%, 20%, 30%, and 40% by weight ceramic were fabricated by solvent casting using DMF as a solvent. Higher thermal stability at the higher ceramic content was indicated by TGA thermograms. A percentage of water uptake and the proton conductivity were increased with blending PAN into PVDF and increasing 5 mol% Sb-TiO<sub>2</sub> contents.

Keywords: PVDF/PAN-5 mol% Sb-TiO<sub>2</sub> composite; Proton exchange membrane fuel cell

#### 5.2 Introduction

Composite membrane, which has the various advantages such as low cost, lightweight, and easier to manufacture than the other materials, is one of the choices for challenging in proton exchange membrane fuel cells to improve its high-temperature performance and substitute for Nafion. These membranes are made with organic polymers containing ceramic fillers because inorganic materials can have high proton conductivity with hydrophilic properties, good chemical and thermal stability, high porosity, and high specific surface areas and organic materials can make membranes elastic and have good mechanical properties with hydrophobic properties. Thus, inorganic/organic composites, which are applicable at higher temperature and in moderate water vapor pressures, are appropriate for electrolyte use [3-5].

In Chen-Yang's work [6], a series of novel solid-type  $\alpha$ - $\text{Al}_2\text{O}_3$ -containing polyacrylonitrile (PAN)-based composite polymer electrolytes (CPE) with high conductivity and high mechanical property at room temperature was prepared. The effect of the addition of  $\alpha$ - $\text{Al}_2\text{O}_3$  on the properties of the PAN-based composite polymer electrolyte was analyzed. The best conductivities obtained at room temperature is  $5.7 \times 10^{-4} \text{ S cm}^{-1}$  from the CPE with 7.5 wt%  $\alpha$ - $\text{Al}_2\text{O}_3$  and 0.6  $\text{LiClO}_4$  per PAN repeat unit.

In 2003 and 2004, Navarra's research [1, 2, 5] reported on the synthesis and the properties of a new microporous, composite proton-conducting gel membrane, formed by swelling a poly(vinylidene)fluoride- poly(acrylonitrile), PVdF/PAN blend-based matrix containing a dispersed  $\text{Al}_2\text{O}_3$  ceramic filler with aqueous acid solutions. It was shown that this membrane had a high and stable conductivity, a proton transport not critically influenced by the relative humidity level, and a projected low cost. Furthermore, new poly-vinylidene fluoride/poly-acrylonitrile (PVdF/PAN) based proton conducting membranes by means of vibrational spectroscopy was investigated in 2005. It was found that a complete phase inversion occurred during the preparation procedure, when the gelling solvents were replaced by an acidic solution, providing the proton conducting property. The uptake of acid was promoted both by the presence of PAN and the ceramic filler,  $\text{Al}_2\text{O}_3$ . No particular interaction between the polymer matrix and the acidic solution could be detected, supporting the picture of an inert matrix entrapping a liquid component. However, the dissociation degree of the acid was decreased due to the spatial confinement in the membrane. By comparing the dissociation degree and the actual amount of acid in the membrane to the conductivity, it was concluded that the limiting factor for the conductivity was the long-range mobility of the protons, which was governed by the morphology of the membrane.

In this study, the weight ratio of PVDF/PAN was 9:1. The PVDF/PAN-5 mol% Sb- $\text{TiO}_2$  composite films were prepared using solvent casting. Microstructure and distribution of ceramic power were observed by SEM and EDX. Higher proton conductivity and higher a percentage of water uptake were found in the film when blending PAN into the PVDF matrix.

## 5.3 Experiment

### 5.3.1 Materials

The Poly(vinylidene fluoride) (PVDF) pellets were given by Solvay (#1008). *N,N*-Dimethyl formamide (DMF) was purchased from Lab Scan. Polyacrylonitrile (PAN) were purchased from S.M. Chemical.

### 5.3.2 PVDF/PAN Blend Film Preparation

Poly(vinylidene fluoride) powders manufactured from Solvay Company (Belgium) (Solef 1008) and Polyacrylonitrile (PAN) purchased from Aldrich Chemical Co. Inc. (USA) were mixed together in DMF solution. The weight ratio of PVDF/PAN was 9:1. The viscous solution was then casted on glass substrate. After the solvent evaporation in a vacuum oven at 60°C for 3 hour, the precursor membranes were washed in distilled water and dried in vacuum to assure the elimination of the solvent.

### 5.3.3 PVDF/PAN-Antimony Modified Titania Composite Preparation

Poly(vinylidene fluoride) powders manufactured from Solvay Company (Belgium) (Solef 1008) and Polyacrylonitrile (PAN) purchased from Aldrich Chemical Co. Inc. (USA) were mixed together in DMF solution at 60°C. The weight ratio of PVDF/PAN was 9:1. For composite preparation, the polymer:solvent ratio was 1:10 w/v. Proportionate quantity of Antimony-modified Titania ceramics powder was added in the polymer solution. It was homogenized by magnetic stirrer. The solution was then cast on glass substrate. After that, the solvent was evaporated in a stove at 60°C for 3 hour under vacuum. Following this method, the composite films of 10%, 20%, 30%, and 40% by weight ceramic were fabricated. The precursor membranes were washed in distilled water and dried in vacuum to assure the elimination of the solvent. The dispersion of ceramic particles was observed by using SEM and EDX-mapping. The composite membranes were tested in order to evaluate the potential use as electrolyte in PEMFCs at high temperature by using TGA, Impedance spectroscopy and Water uptake. Lloyd Universal Testing machine were carried out to measure the mechanical properties of the thin films.

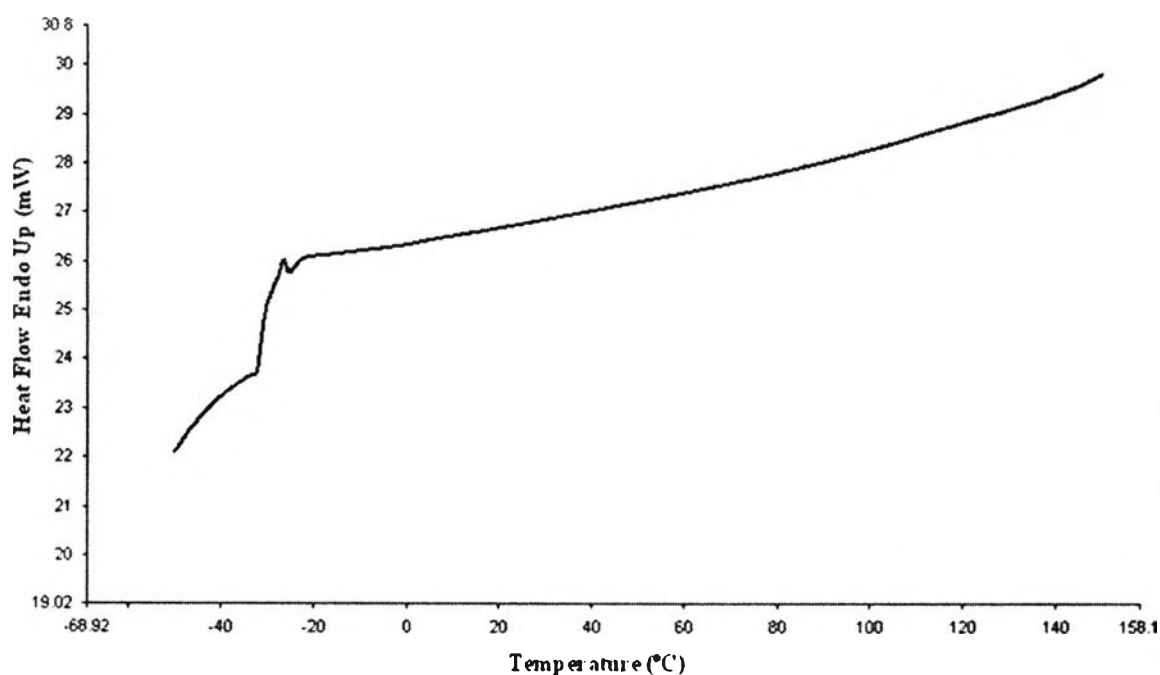
#### 5.3.4 Characterization

The glass transition temperature of polyvinylidene fluoride/polyacrylonitrile blend film was measured by using differential scanning calorimeter 7, DSC 7 (Perkin Elmer). The distribution of ceramic powders in composites was observed using a Hitachi/S-4800 field emission scanning electron microscope and the doped Sb species were identified by LINK ISIS series 300 for Energy dispersive X-ray (EDX) analysis. Thermal stabilities of composite film were investigated by Thermo gravimetric Analyzer, Perkin-Elmer. TG-DTA pyres diamond. Mechanical properties of the thin films were investigated by using a Model LRX Lloyd Universal Testing machine following ASTM D882. The water uptake (%W) was measured by soaking the samples in the water. The impedance of the samples was measured by using impedance analyzer (Hewlett Packard., model 4194A) in impedance (Z) mode, with frequency from 1 kHz to 10 MHz.

### 5.4 Results and Discussion

#### 5.4.1 Miscible Blend of PVDF/PAN

The glass transition temperature of polyvinylidene fluoride/polyacrylonitrile blend film in the weight ratio of 9:1 was measured by using differential scanning calorimeter at a heating rate of 10 °C/min. DSC thermogram of the samples was characterized as function of temperature in range of -50 °C to 150 °C as shown in Figure 5.1.



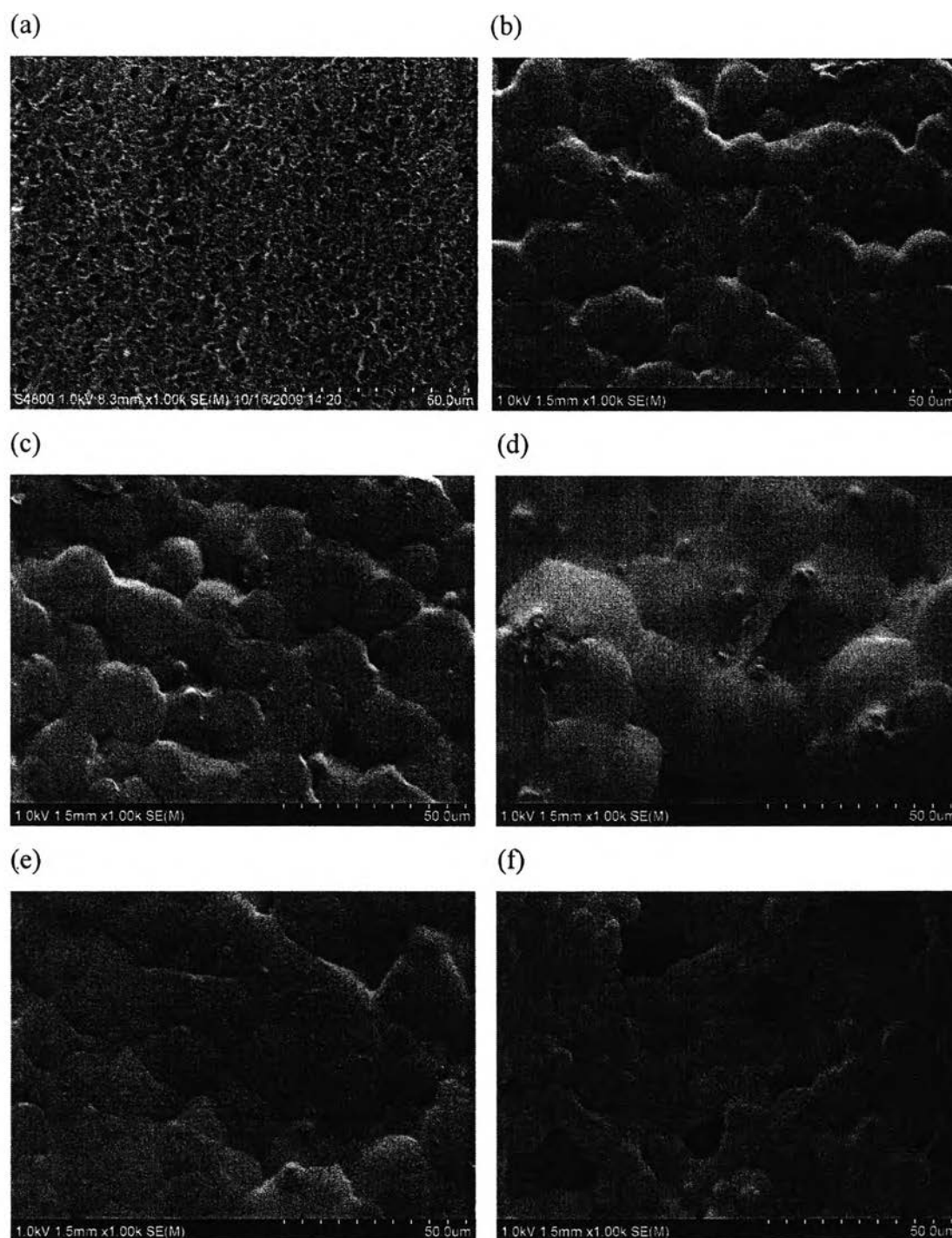
**Figure 5.1** DSC Thermograms of polyvinylidene fluoride/polyacrylonitrile blend film in the weight ratio of 9:1 at a heating rate of 10 °C/min from -50 °C to 150 °C.

From the results, the glass transition temperature of blend film is -28.91 °C. The blend film had only one glass transition temperature. So, polyvinylidene fluoride/polyacrylonitrile blend film in the weight ratio of 9:1 is miscible blend.

#### 5.4.2 PVDF/PAN-5 mol% Antimony Modified Titanium Dioxide (5 mol%Sb-TiO<sub>2</sub>) Composite Film in Various Amounts of Ceramic Powder

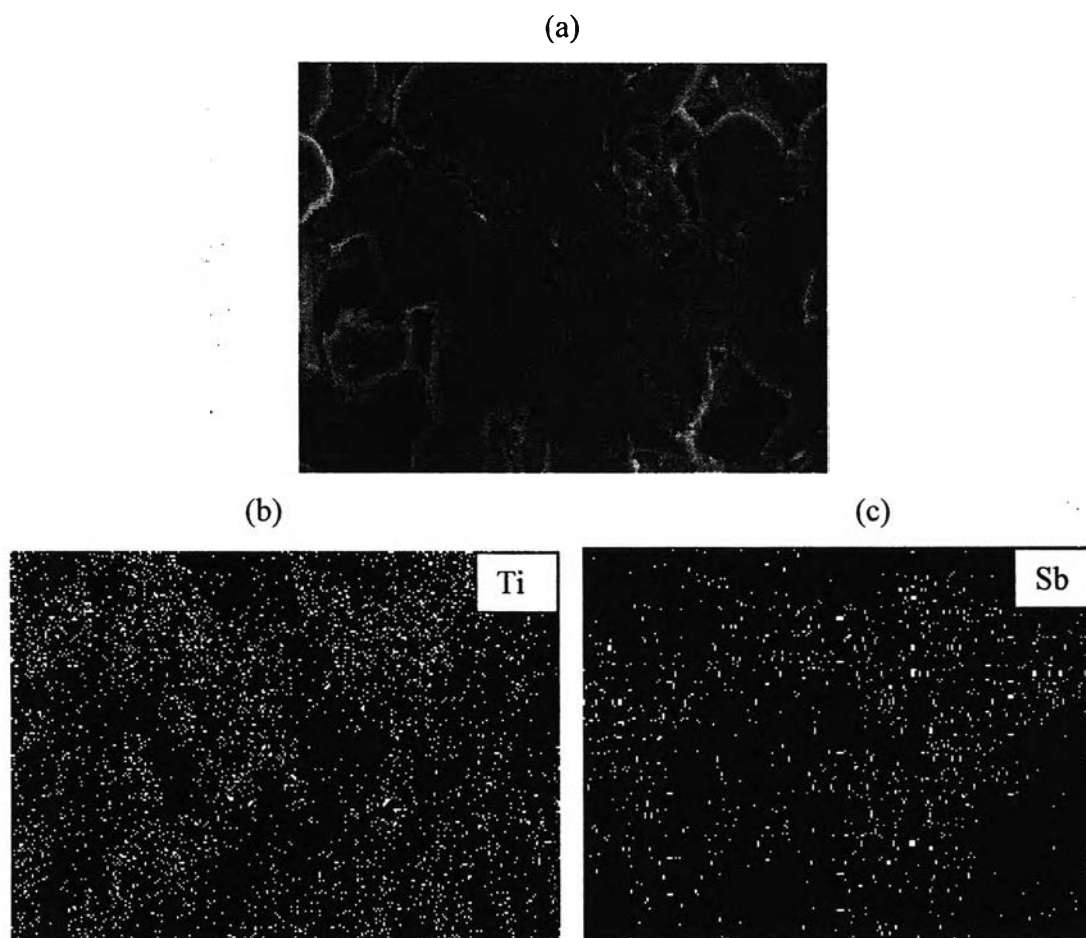
##### 5.4.2.1 *SEM/EDX Analysis of PVDF/PAN-5 mol%Sb Doped TiO<sub>2</sub> Thin Films*

SEM micrograph of the composites containing 10, 20, 30, and 40 wt% ceramic filler which fine powder was dispersed in a PVDF/PAN matrix were shown in Figures 5.2. The composites displayed the microstructure of larger agglomeration in PVDF/PAN matrix when amounts of ceramic increased. However, at higher ceramic content, the flexibilities of composite films were reduced due to the high stiffness of ceramic powder.

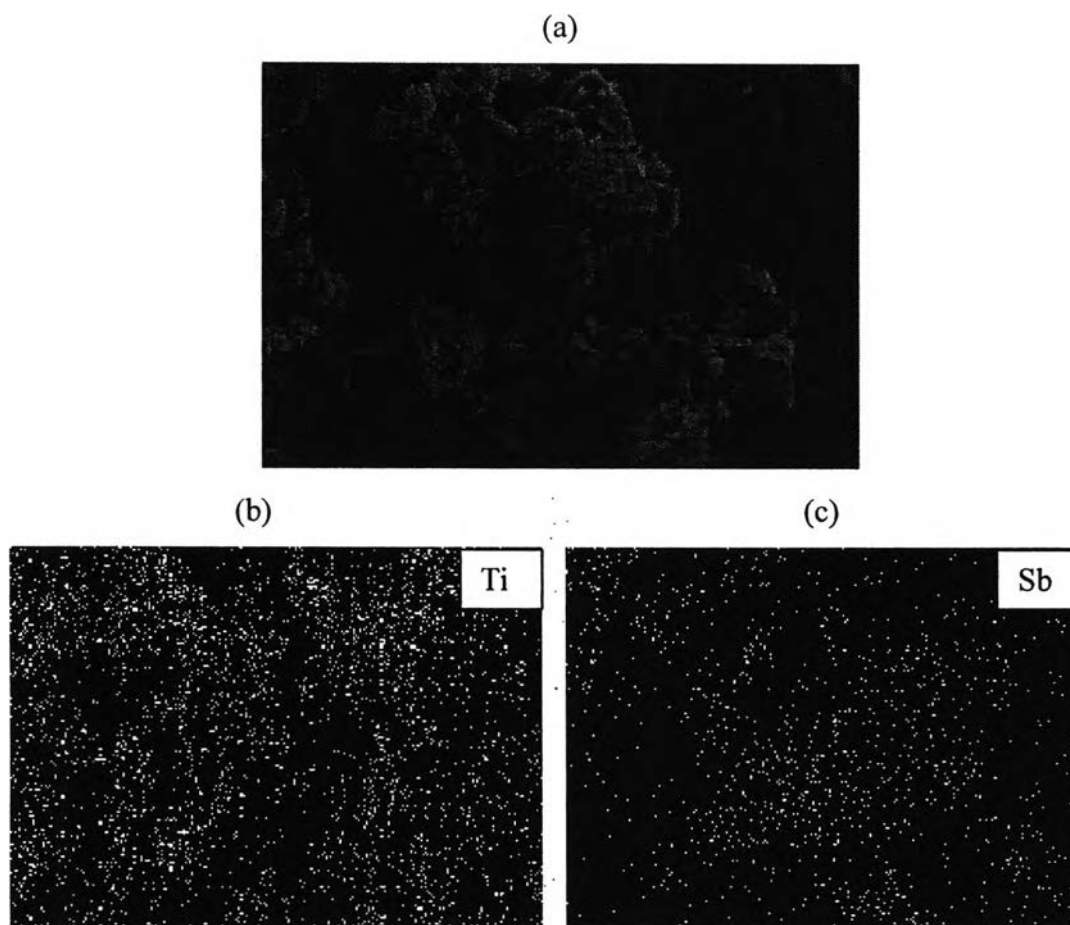


**Figure 5.2** SEM images of (a) PVDF cast film, (b) PVDF/PAN blend film, (c) PVDF/PAN-10%wt of 5 mol%Sb-TiO<sub>2</sub>, (d) PVDF/PAN-20%wt of 5 mol%Sb-TiO<sub>2</sub>, (e) PVDF/PAN-30%wt of 5 mol%Sb-TiO<sub>2</sub>, (f) PVDF/PAN-40%wt of 5 mol%Sb-TiO<sub>2</sub>.

In addition, EDX analysis was used to observe the distribution and dispersion of ceramic powder in the PVDF/PAN matrix. EDX Sb and Ti-mapping photographs show the homogeneous and uniform distribution of Sb-TiO<sub>2</sub> ceramic in PVDF/PAN matrix as presented in Fig. 5.3, 5.4, 5.5, and 5.6.

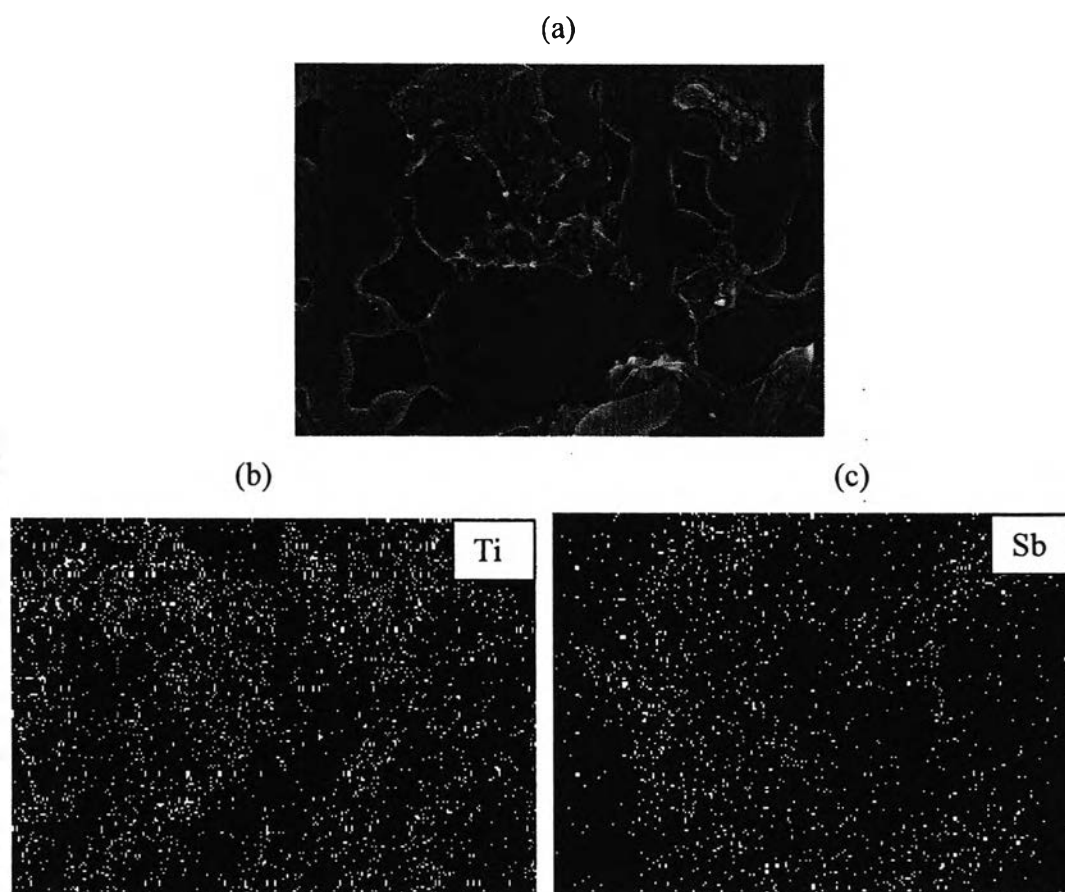


**Figure 5.3** (a) SEM image (scale bar = 6  $\mu\text{m}$ ), (b) EDX Ti-mapping photograph, (c) EDX Sb-mapping photograph of PVDF/PAN-10%wt of 5 mol% Sb-TiO<sub>2</sub>.

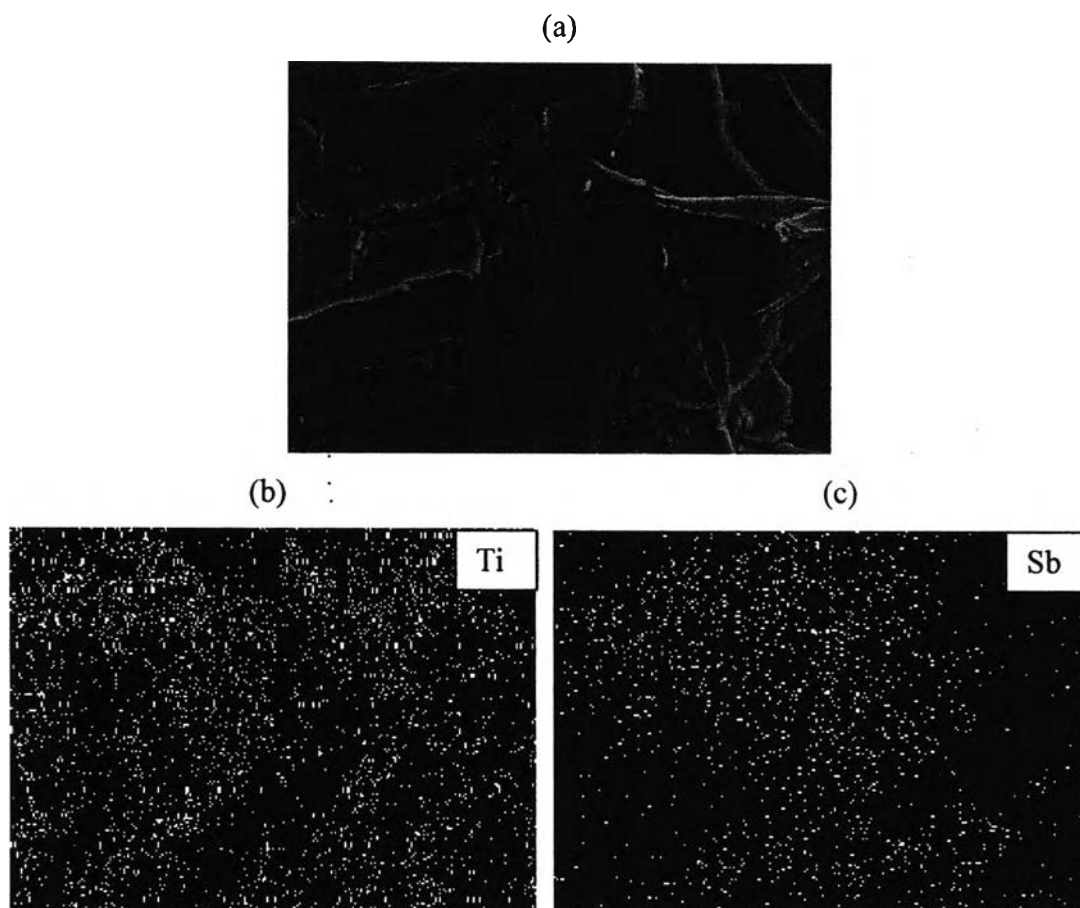


**Figure 5.4** (a) SEM image (scale bar = 6 μm), (b) EDX Ti-mapping photograph, (c) EDX Sb-mapping photograph of PVDF/PAN-20%wt of 5 mol% Sb-TiO<sub>2</sub>.





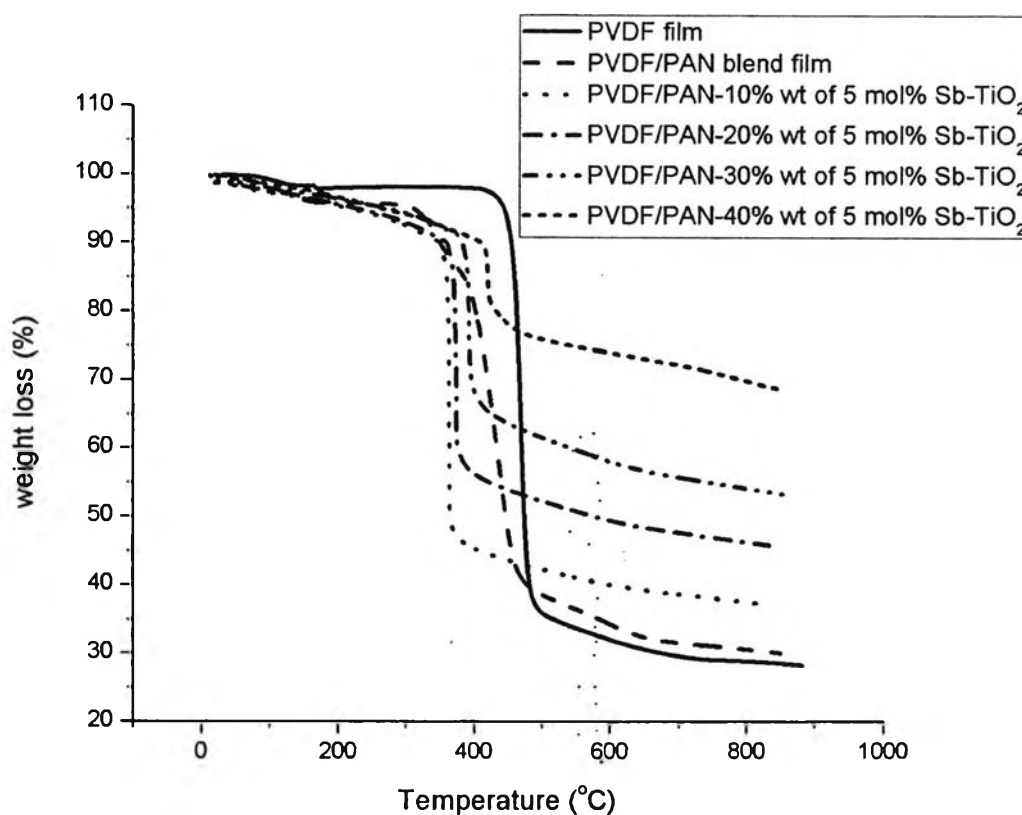
**Figure 5.5** (a) SEM image (scale bar = 6  $\mu\text{m}$ ), (b) EDX Ti-mapping photograph, (c) EDX Sb-mapping photograph of PVDF/PAN-30%wt of 5 mol% Sb-TiO<sub>2</sub>.



**Figure 5.6** (a) SEM image (scale bar = 6  $\mu\text{m}$ ), (b) EDX Ti-mapping photograph, (c) EDX Sb-mapping photograph of PVDF/PAN-40%wt of 5 mol%Sb-TiO<sub>2</sub>.

#### 5.4.2.2 TGA Analysis of PVDF/PAN-5 mol%Sb Doped TiO<sub>2</sub> Thin Films

The graphic of weight loss versus temperature for PVDF, PVDF/PAN blend and PVDF/PAN-5 mol%Sb doped TiO<sub>2</sub> composite as shown in Figure 5.7. The first mass loss at temperature below 150 °C indicates the presence of water. The second mass loss at temperature around 200-300 °C shows the presence of PAN in PVDF matrix and the third mass loss at approximately near 400 °C presents the decomposition of PVDF. TGA thermograms showed that the incorporation of 5mol%Sb-TiO<sub>2</sub> ceramic in the PVDF/PAN films enhances the higher residue of composite when compared to the pure PVDF and PVDF/PAN blend film.



**Figure 5.7** TGA thermograms of PVDF cast film, PVDF/PAN blend film and PVDF/PAN-5 mol%Sb doped  $\text{TiO}_2$  cast films.

#### 5.4.2.3 Mechanical Properties of PVDF/PAN-5 mol%Sb Doped $\text{TiO}_2$ Thin Films

Tensile properties were measured in order to evaluate the stiffness and strength of the thin films. With blending PAN into PVDF matrix, the Young's Modulus of films increased while the percentage strain at break and the stress at break decreased as it can be seen in the Table 5.1. PAN is the amorphous polymer and has high glass transition temperature ( $85\text{ }^\circ\text{C}$ ). So, it can make the blend films quite brittle and stiff.

**Table 5.1** Mechanical properties of PVDF cast film, PVDF/PAN blend film and PVDF/PAN-5 mol%Sb doped TiO<sub>2</sub> thin films

Samples	Young's Modulus (MPa)	Stress at Break (MPa)	Percentage Strain at Break
PVDF Cast Film	272.42 ± 2.45	24.66 ± 3.38	17.00 ± 1.26
PVDF/PAN Blend Film	490.36 ± 3.43	19.843 ± 2.25	11.235 ± 1.57
PVDF/10%wt of 5 mol%Sb-TiO <sub>2</sub>	536.98 ± 4.56	13.4607 ± 2.18	9.5231 ± 1.88
PVDF/20%wt of 5 mol%Sb-TiO <sub>2</sub>	597.65 ± 3.98	8.4355 ± 1.94	6.8906 ± 2.03
PVDF/30%wt of 5 mol%Sb-TiO <sub>2</sub>	667.47 ± 2.73	6.3417 ± 1.53	3.9087 ± 1.54
PVDF/40%wt of 5 mol%Sb-TiO <sub>2</sub>	743.84 ± 3.55	3.2356 ± 1.76	1.0244 ± 1.77

#### 5.4.2.4 Water Uptake Testing of PVDF/PAN-5 mol%Sb Doped TiO<sub>2</sub> Thin Films

The results of water uptake testing at room temperature exhibit that percentage of water uptake of blend films increased with blending PAN into PVDF, because of the hydrophilicity of PAN, as shown in Table 5.2. This increase may be due to the polar group (–CN group) in the structure of PAN.

**Table 5.2** Water uptake of PVDF cast film, PVDF/PAN blend film and PVDF/PAN-5 mol%Sb doped TiO<sub>2</sub> thin films

Samples	Percentage of Water Uptake
PVDF Cast Film	4.66
PVDF/PAN Blend Film	10.01
PVDF/10%wt of 5 mol%Sb-TiO <sub>2</sub>	12.34
PVDF/20%wt of 5 mol%Sb-TiO <sub>2</sub>	14.27
PVDF/30%wt of 5 mol%Sb-TiO <sub>2</sub>	17.66
PVDF/40%wt of 5 mol%Sb-TiO <sub>2</sub>	22.21

5.4.2.5 Proton Conductivity Measurement of PVDF/PAN-5 mol%Sb Doped TiO<sub>2</sub> Thin Films

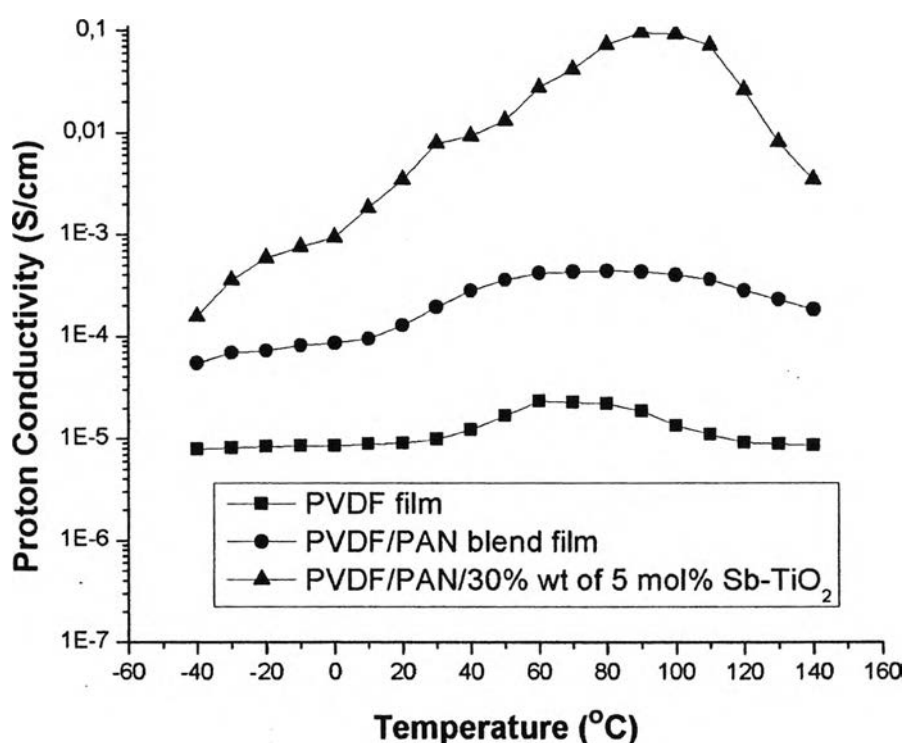
The results of resistance and proton conductivity of all membranes at room temperature after soaking in 6M H<sub>2</sub>SO<sub>4</sub> aqueous solution for 24 hours were demonstrated in Table 5.3. The proton conductivity of membranes was enhanced by blending PVDF with PAN because PAN is the polar polymer, leading to obtain higher water adsorption ability and resulting in an increase of proton conductivity.

**Table 5.3** Resistance and conductivity at 25 °C of PVDF cast film, PVDF/PAN blend film and PVDF/PAN-5 mol%Sb doped TiO<sub>2</sub> thin films

Samples	Resistance (Ohms)	Conductivity (S/cm)
PVDF Cast Film	1183.74	$9.04 \times 10^{-6}$
PVDF/PAN Blend Film	105.97	$1.29 \times 10^{-4}$
PVDF/PAN-10%wt of 5 mol%Sb-TiO <sub>2</sub>	67.52	$2.34 \times 10^{-4}$
PVDF/PAN-20%wt of 5 mol%Sb-TiO <sub>2</sub>	34.57	$8.32 \times 10^{-4}$
PVDF/PAN-30%wt of 5 mol%Sb-TiO <sub>2</sub>	10.11	$3.50 \times 10^{-3}$
PVDF/PAN-40%wt of 5 mol%Sb-TiO <sub>2</sub>	0.19	$9.25 \times 10^{-2}$

From all of these results, the optimum %wt of ceramic in PVDF/PAN matrix should be 30%wt due to the high percentage of water uptake, high proton conductivity and good flexibility of this film. The temperature dependence of proton conductivity of PVDF film, PVDF/PAN blend film and PVDF/PAN-30%wt of 5 mol%Sb-TiO<sub>2</sub> composite were investigated from -40 °C to 140 °C in Figure 5.8. From these graphs, it should be observed that the proton conductivity of PVDF/PAN composite film increased rapidly ( $\sim 10^{-4}$  S/cm to  $\sim 10^{-1}$  S/cm) in the long range of temperature (-40 °C to 90 °C) before decreased rapidly ( $\sim 10^{-1}$  S/cm to  $\sim 10^{-3}$  S/cm) in the short range of temperature (90 °C to 140 °C). The

behavior of conductivity decreasing above 100 °C suggests the higher dehydration of the membrane with higher temperature. However, the composite blend film can keep the proton better than PVDF/PAN blend film and pure PVDF film due to the pore structure of ceramic powder. At 90 °C, the proton conductivity for the PVDF/PAN-30%wt of 5 mol%Sb-TiO<sub>2</sub> composite film is 0.0967 S/cm, which is the maximum conductivity value.



**Figure 5.8** The temperature dependence of proton conductivity of PVDF film, PVDF/PAN blend film and PVDF/PAN-30%wt of 5 mol%Sb-TiO<sub>2</sub> films.

## 5.5 Conclusion

The PVDF/PAN-5 mol% Sb-TiO<sub>2</sub> composites were successfully fabricated. The blending PAN into PVDF in the composite shows enhancement of a percentage of water uptake and proton conductivity compared to pure PVDF film. PAN is the polar polymer, leading to obtain higher water adsorption ability and resulting in an increase of proton conductivity. However, PAN is the amorphous polymer and has

high glass transition temperature. So, it can make the blend films quite brittle and stiff. The combination of PAN and 5 mol% Sb-TiO<sub>2</sub> ceramic causes the membranes have higher water adsorption and higher proton conductivity than PVDF/5 mol% Sb-TiO<sub>2</sub> composite and pure PVDF membrane. The optimum % wt of ceramic in PVDF/PAN composite is 30 % wt due to the good flexible film and 3 orders of magnitude higher than the pure PVDF film.

## 5.6 Acknowledgement

The authors would like to thank Dr. Pitak Laoratanakul and MTEC staffs for useful assistance and instruments for characterizations. The partial funding of research work was provided by Polymer Processing and Polymer Nanomaterials Research Unit, National Science and Technology Development Agency (NSTDA), Thailand and National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

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