



## CHAPTER IV

### MECHANICAL STRETCHING EFFECT OF SOLUTION-CASTED PVDF FILM

#### 4.1 Abstract

This work studied stretching effect of solution-casted film to film morphologies and dielectric properties. PVDF film of the thickness range of 70-90  $\mu\text{m}$  was fabricated from *N,N*-dimethylformamide (DMF)-solution casting technique at 60°C, the casted film was stretched at the ratio of 2, 4 and 6 by mechanical stretching machine at 90°C. The film morphologies of all samples were observed by Scanning Electron Microscope (SEM) and dielectric properties were investigated by Impedance/Gain-Phase Analyzer. SEM images showed that the casted film yielded high porosity which was reduced by applying mechanical stretching and circular porous shape of the original casted film was changed to ellipsoid structure at all stretching ratio. However, the dielectric results of casted film showed higher dielectric constant than those of all stretched films but its dielectric loss was improved as increasing stretching ratio. By applying mechanical stretching to casted film, the high  $\beta$ -phase content was lowered but less porosity improved the dielectric loss.

Keywords: Stretching effect; Morphology; Dielectric properties

#### 4.2 Introduction

Polyvinylidene fluoride (PVDF) is known for its interesting piezo-, pyro-, and ferroelectric properties, which allow important electro-optical, electro-mechanical and biomedical applications. PVDF has a chemical composition of  $(\text{CH}_2\text{-CF}_2)_n$  and is more formally known as 1,1 difluoro-ethylene. It is a semi crystalline polymer with was typically 50 to 60% crystalline depending on thermal and processing history and has at least four crystal phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ), of which at least three are polar [Harrison *et al.*, 2001]. However, two main crystals which have recently attracted

much interest for their pyro- and piezoelectric are  $\alpha$  phase and  $\beta$  phase [Ye *et al.*, 2004]. Non-polar  $\alpha$  phase, chain is in a sequence of alternating trans and gauche sequences with a helical (TGTG') configuration [Takahashi *et al.*, 1993], resulting in no net dipole. The  $\beta$ -phase crystal has all trans planar zigzag (TTTT) conformation that results in the most polar phase among other crystals, being used extensively in piezoelectric, pyroelectric and ferroelectric applications [Broadhurst *et al.*, 1984, Furukawa *et al.*, 1990, Broadhurst *et al.*, 1978]. This phase can be obtained mainly by two techniques: by mechanical stretching from the  $\alpha$ -phase or directly from solution. The most common way for obtaining  $\beta$ -PVDF is by mechanical stretching of  $\alpha$ -phase films at a given temperature. Conversion of  $\gamma$ -phase from melt crystallization into  $\beta$ -phase takes place at stretching temperatures below 100 °C (70-100 °C), at a stretching ratio of about 3–5. Higher stretching temperatures reduce the phase conversion efficiency and conversion into  $\beta$ -phase takes place only for stretch ratios above 5 [Khomami *et al.*, 1988, Salimi *et al.*, 2003]. Another way is unoriented films exclusively in the  $\beta$ -phase can be obtained from the crystallization of PVDF from solution with *N,N*-dimethylformamide (DMF) or dimethylacetamide (DMA) at temperatures below 70°C. Predominant phase strongly depends on the evaporation temperature of the solvent. Temperatures below 70°C provided exclusively the  $\beta$  phase. At increasing temperatures formation of the  $\alpha$  phase commenced and became predominant above 110°C [Gregorio *et al.*, 2004]. Usually, the cast films of pure PVDF exclusively in the  $\beta$ -phase possess a high degree of porosity, which makes them opaque and fragile with a decrease of the mechanical and electrical properties. Those pores formed in the films, which can cause a degradation of the electrical properties and do not allow the poling of the films. This limits the application for the piezo-, pyro- and ferroelectric effects [Gregorio *et al.*, 1999, Gregorio *et al.*, 2006, Sencadas *et al.*, 2006].

This present investigation is aimed to study how the mechanical stretching of PVDF film, fabricated from solution-casting technique with *N,N*-dimethylformamide affect the surface morphology and  $\beta$ -crystalline phase content in the film. And also dielectric properties were discussed as the function of frequencies at room temperature.

## 4.3 Experiment

### 4.3.1 Materials

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

### 4.3.2 Preparation of PVDF film

PVDF film was fabricated by the solution casting which PVDF pellets dissolved in DMF solution at 60 °C, the initial concentration was 20 %w/v. The viscous solution was then cast on glass substrate. After the solvent evaporation in a stove at 60 °C for 1 hour under vacuum, the sample films of 70-90 μm thickness was obtained.

### 4.3.3 Stretching of PVDF film

PVDF film from casting technique was stretched by mechanical testing machine (Universal testing machine, Lloyd) at 90°C to obtain film at different stretching ratio at constant stretching rate of 50 mm/min.

### 4.3.4 Characterization

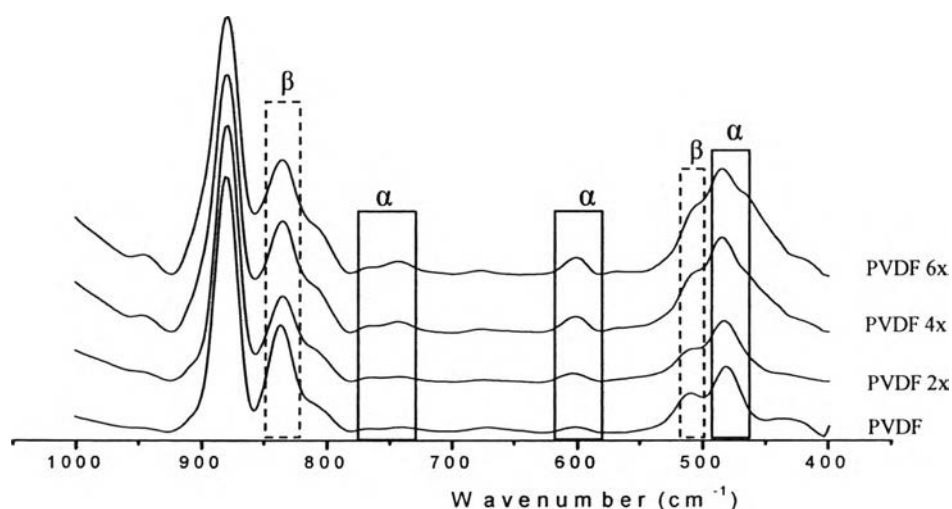
β crystalline phase for PVDF were measured and investigated by Fourier Transformation Infrared Spectrophotometer (FTIR) and X-ray diffraction (Rigaku, model Dmax 2002). Thermal behavior of PVDF films were performed by a differential scanning calorimeter 7, DSC 7 (Perkin Elmer). Microstructures and film morphology of BT/BST were performed by a scanning electron microscope (JEOL, model JSM 2590). Finally, the dielectric properties of PVDF films at different stretching ratio were measured using impedance/gain-phase analyzer (Hewlett Packard., model 4194A) in parallel capacitance ( $C_p$ ) mode, with frequency from 1 kHz to 10 MHz.

## 4.4 Result and Discussion

### 4.4.1 Phase Characterization

Two important phases, α and β phase, of casted PVDF film and stretched PVDF film were characterized and calculated by using vibrational spectra of FTIR technique. The characteristic infrared bands of the β crystalline phase for PVDF

were  $839\text{ cm}^{-1}$  and those of the  $\alpha$  crystalline phase were  $763$  and  $976\text{ cm}^{-1}$  [Kim, *et al.*, 1998]. The complete predominated for  $\beta$ -crystalline phase was found in DMF solution-casted PVDF while  $\beta$ -crystalline phase decreased in all stretched film as shown in Figure 4.1. The casted film yielded higher  $\beta$ -crystalline phase than those of all stretched films. According to Figure 4.1, the absorption band at  $840$  and  $510\text{ cm}^{-1}$  which is characteristic of  $\beta$ -crystalline phase decreased when stretching ratio increased while characteristic of  $\alpha$  crystalline phase, the absorption band at  $763$ ,  $600$  and  $490\text{ cm}^{-1}$ , showed increasing in absorbance. For the DMF solution-casted PVDF, polar solvent can reduce the energy required to form a polar crystal ( $\beta$  crystalline phase) [Salimi *et al.*, 2004] but this high  $\beta$ -crystalline phase was affected when mechanical stretching was applied. Absorption bands which were shown in Figure 4.1 were used to calculate the changes in the  $\beta$ -crystalline phase in all films. Appearances of absorption band at  $763$  and  $840\text{ cm}^{-1}$ , feature of  $\alpha$ - and  $\beta$ -crystalline phases, were used to calculate  $\beta$  crystalline phase content ( $F(\beta)$ ) for all PVDF films. The calculated  $F(\beta)$  of solution-casted and stretched film with different stretching ratio were summarized in Table 4.1. The  $F(\beta)$  decreased as the draw ratio increased because all-*tran* (*ttt*) planar zigzag  $\beta$ -crystalline phases of original casted film was distorted by mechanical stretching. For DMF solution-casted PVDF, the highest value of  $F(\beta)$  was observed.

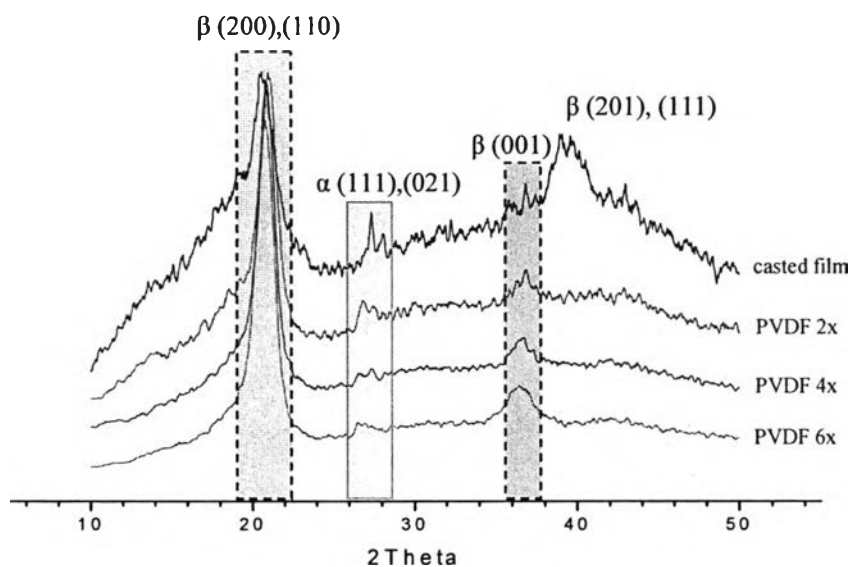


**Figure 4.1** FTIR spectra of DMF solution-casted PVDF and stretched PVDF at the different draw ratio from 2 to 6.

**Table 4.1** The variations of F ( $\beta$ ) of solution-casted PVDF and stretched PVDF by increasing stretching ratio at constant drawn rate of 50 min/mm

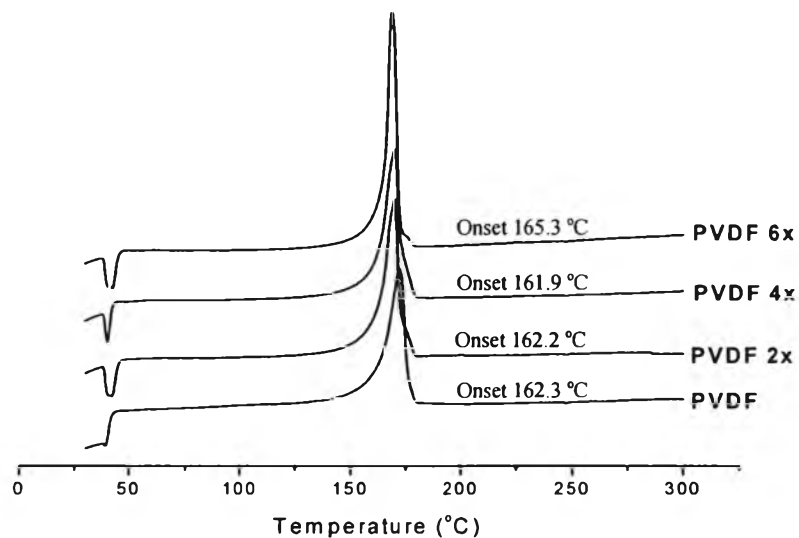
Material	$\beta$ -phase content, F ( $\beta$ ) (%)
PVDF	95.22
PVDF 2x	92.72
PVDF 4x	92.62
PVDF 6x	92.11

XRD measurement was performed to identify the crystal phase of PVDF films. Fig. 4.2 showed the x-ray diffraction patterns of casted and stretched films. From XRD pattern, casted film showed the peaks in  $2\theta$  Bragg angle with values of 20.4, 36.7 and 40 corresponding to  $\beta$ -crystalline phase. Nevertheless, the casted film still had little peak of  $\alpha$ -crystalline phase at  $27^\circ$  [Ye, Y., 2004]. By stretching the casted film the peak around  $40^\circ$  which refer to  $\beta$ -PVDF resulting from molecular defects caused by head-head and tail-tail (HHTT) sequences [Lovinger *et al.*, 1987] disappeared because of stretching effect but all stretched film remained peak around  $27^\circ$ , referring to  $\alpha$ -crystalline phase. This XRD result can be concluded that casted film and all stretched film yielded both  $\beta$  and  $\alpha$  phase and mechanical stretching affect to original crystalline of film.



**Figure 4.2** X-ray diffraction patterns of casted and stretched film of PVDF.

DSC thermograms of all samples were characterized as function of temperature in range of 30°C to 300°C. Only endothermic peak in the temperature range from 150°C to 170°C was detected in all films as shown in Figure 3, corresponding to melting temperature of semicrystalline PVDF. However, the melting temperature seem to be constant for all sample that is general and particular for PVDF [Nakagawa *et al.*, 1973]. Due to melting temperature relates to lamellae thickness, mechanical stretching affects the crystal structure by showing a little bit changing of crystallinity in stretched films which can be seen in table 2, the melting enthalpy and consequently the degree of crystallinity of PVDF almost constant with increasing applied stretching.



**Figure 4.3** DSC Thermograms at a heating rate of 10°C/min from 30°C to 300°C.

**Table 4.2** Melting temperature (onset), Heat of fusion and Crystallinity of solution-casted PVDF and stretched PVDF

Material	Melting Temperature Onset (°C)	heat of fusion $\Delta H_m$ , J/g	% Crystallinity
PVDF	162.3	65.5	62.6
PVDF 2x	162.2	65.9	63.1
PVDF 4x	161.9	64.4	61.6
PVDF 6x	165.3	66.3	63.4

The degree of crystallinity was measured as the ratio between  $\Delta H_m$  and  $\Delta H_0$ , as following equation

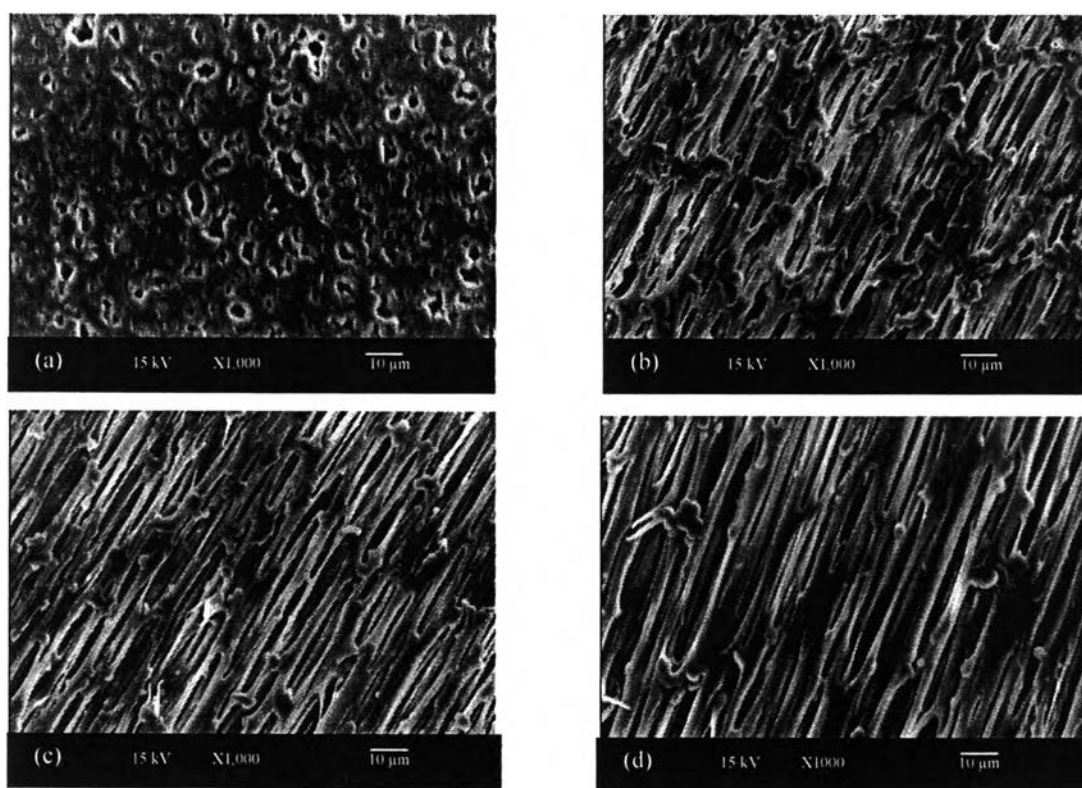
$$\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_0} \times 100$$

where  $\Delta H_m$  is the melting enthalpy of the material under study and  $\Delta H_0$  is the melting enthalpy of totally crystalline material ( $\Delta H_0 = 104.50$  J/g for PVDF) [Teyssedre *et al.*, 1993 Nakagawa *et al.*, 1979].

From the DSC results stretching  $\beta$ -PVDF film at  $90^\circ\text{C}$  did not significantly affect to amount of crystallinity (as shown in Table 4.2) of films but the  $\beta$ -crystalline phase was distorted as shown in FTIR and XRD result, indicated reducing of  $\beta$ -phase content with increasing of stretching ratio.

#### 4.4.2 Film Morphology

SEM micrographs of all fabricated PVDF films were shown in Fig 4.4. Films from solution casting expressed porous generated from solvent evaporate and led to defect on the surface of film. By applying mechanical stretching at suitable temperature, the thinner film was obtained and also porous is changed to ellipsoid shape which affect to film density as shown in table 4.3. The average density of film was increased when stretching ratio was increased.



**Figure 4.4** SEM micrographs of (a) solution-casted PVDF, (b) stretched PVDF 2x, (c) stretched PVDF 4x and (d) stretched PVDF 6x.

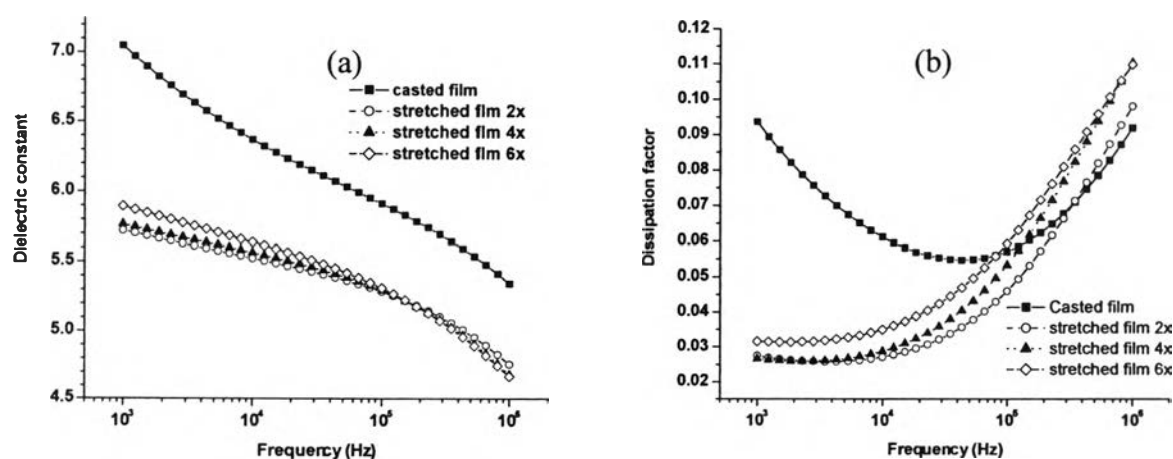


**Table 4.3** Average density of solution-casted PVDF and stretched PVDF with increasing stretching ratio at constant drawn rate of 50 min/mm

Material	Average density (g/cc)
PVDF	1.75
PVDF 2x	1.77
PVDF 4x	1.83
PVDF 6x	2.05

#### 4.4.3 Dielectric Properties

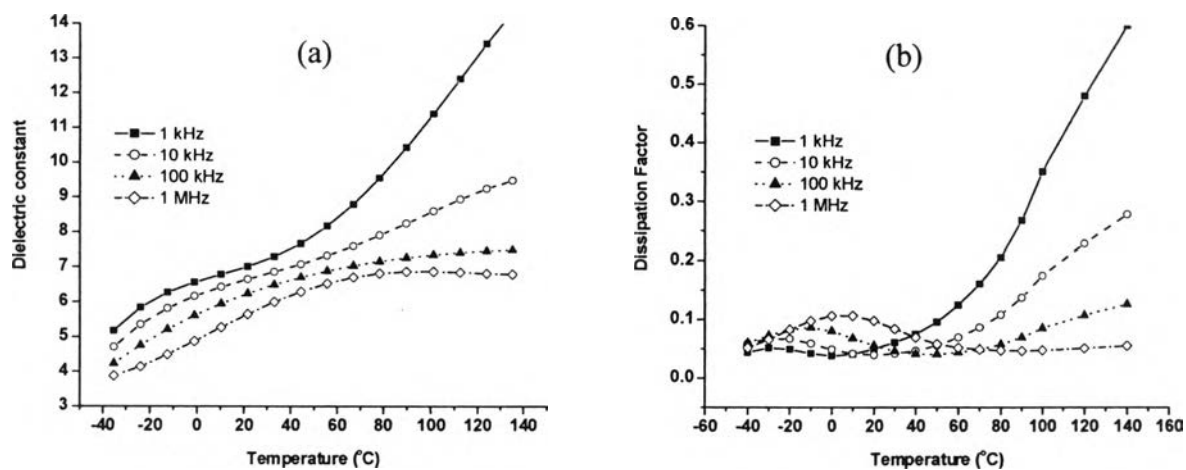
The variations in the dielectric constant and dielectric loss with frequency for the PVDF were shown in Fig. 4.5. The dielectric constants of casted PVDF film were higher than those of all stretched PVDF (as shown in Figure 4.5) because of its high  $\beta$ -phase content which obtained from solution-casting technique. But the solution casted film show high degree of porosity as shown in Figure 4.4 (a), which make them opaque and fragile [Botelho *et al.*, 2008], resulting in higher dissipation factor than those of all stretched films as shown in Figure 4.5 (b).



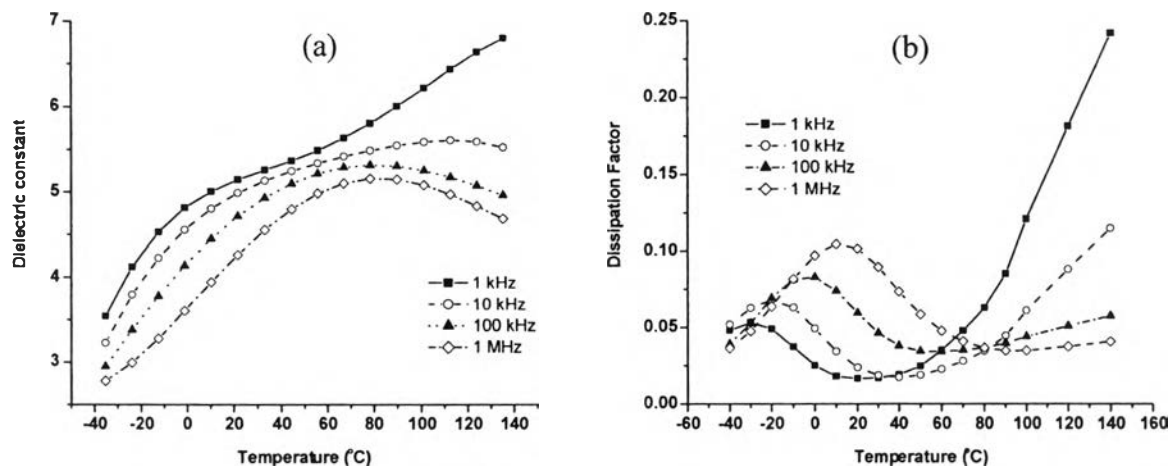
**Figure 4.5** The frequency dependence of (a) the dielectric constant and (b) dissipation factor of casted and stretched PVDF at room temperature.

High porosity of casted film was reduced by mechanical stretching at suitable temperature but this affected to  $\beta$ -phase content of film, leading to decreasing of dielectric constant but not dissipation factor.

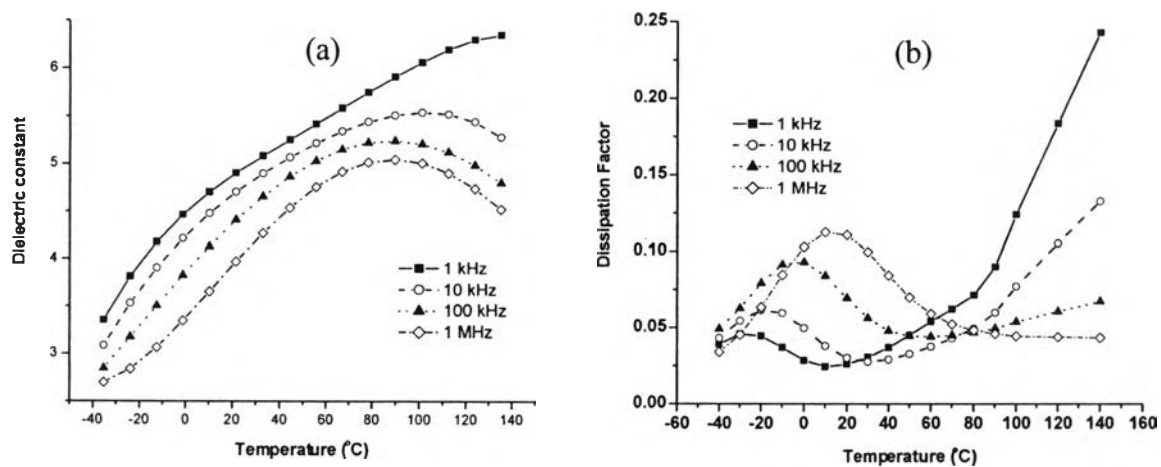
The variations in dielectric constant with temperature for casted film and all stretched film at different frequency were shown in Fig 4.6 to Fig 4.9. The dielectric constant did not remain constant with temperature because PVDF showed relaxation process as slipping of molecule PVDF while increasing temperature at all stretching ratios. The pattern of dissipation factor of all samples showed almost the same which refer that mechanical stretching did not change the mechanism of molecular relaxation despite PVDF film from solution-casting technique was stretched up to stretching ratio 6:1 at 90°C.



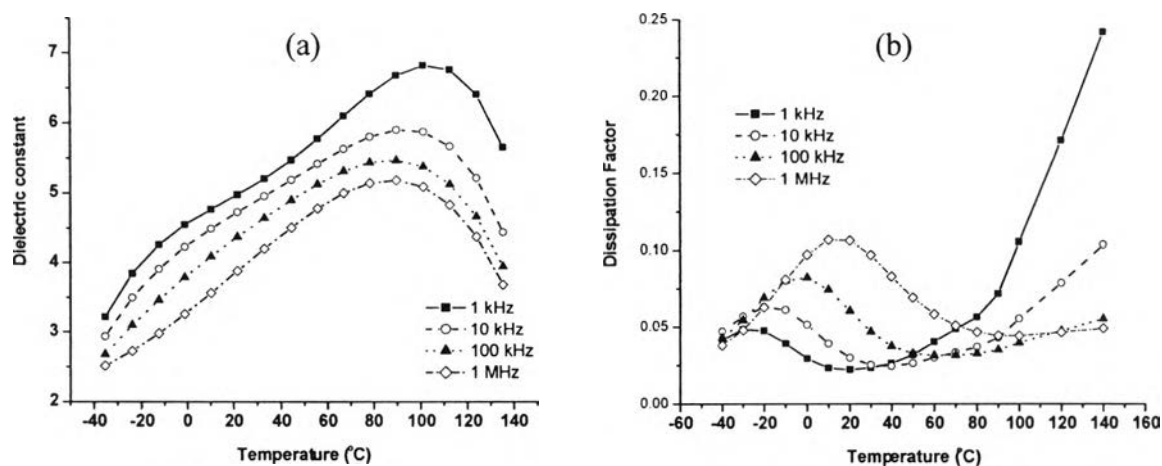
**Figure 4.6** The temperature dependence of (a) the dielectric constant and (b) dissipation factor of solution-casted film at 1 kHz, 10 kHz, 100 kHz and 1 MHz.



**Figure 4.7** The temperature dependence of (a) the dielectric constant and (b) dissipation factor of PVDF 2x at 1 kHz, 10 kHz, 100 kHz and 1 MHz.



**Figure 4.8** The temperature dependence of (a) the dielectric constant and (b) dissipation factor of PVDF 4x at 1 kHz, 10 kHz, 100 kHz and 1 MHz.



**Figure 4.9** The temperature dependence of (a) the dielectric constant and (b) dissipation factor of PVDF 6x at 1 kHz, 10 kHz, 100 kHz and 1 MHz.

#### 4.5 Conclusion

The  $\beta$  crystalline phase of PVDF films made from DMF solution-casting technique had been characterized by Fourier Transform Infrared Spectroscopy (FTIR). It can be calculated that  $F(\beta)$  value is highest in original casted film. However, SEM micrographs show defect of PVDF film fabricated from solution casting which showed that the casted film contained high porosity which made unwish high dielectric loss. Nevertheless, degree of porosity of PVDF casted film was reduced in stretched PVDF films as the spherical voids inside the casted film were transformed to ellipsoidal voids—decreasing of air volume. Consequently, stretched PVDF film showed the lower dielectric constant but the improvement in dielectric loss as effect of less  $\beta$ -phase content and less porosity. Decreasing of  $\beta$  crystalline phase can be confirmed by XRD diffraction as the stretching ratio increase. Moreover, the dielectric results showed that the dielectric constant of all films were temperature dependant and molecular relaxation has not be affected by mechanical stretching (up to stretching ratio 6:1)

#### 4.6 Acknowledgements

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