



CHAPTER II BACKGROUND & LITERATURE REVIEW

2.1 Dielectric Constant

A dielectric material is a substance that is a poor conductor of electricity, but an efficient supporter of electrostatic fields. If the flow of current between opposite electric charge poles is kept to a minimum while the electrostatic lines of flux are not impeded or interrupted, an electrostatic field can store energy [Lines M E and Glass A M, (1979)] that can be calculated in this equation:

$$\epsilon = \frac{Cd}{\epsilon_0 A} \quad (1)$$

Where C is the capacitance (F), ϵ_0 the free space dielectric constant value (8.85×10^{-12} F/m), A the capacitor area (m^2), and d the thickness of specimens. In this research related to equations that required increasing piezoelectric coefficient, so dielectric is most important parameter because it directly relates to piezoelectric coefficient as following equations:

$$D = \epsilon KE \quad (2)$$

Where ϵ is dielectric constant, D is dielectric displacement, K is relative constant between electric field with polarization of material, and E is electric field

$$d = D/T \quad (3)$$

Where d is piezoelectric coefficient, D is dielectric displacement, T is stress. According to this equation at a higher level of “d” it would be beneficial for piezoelectric or ferroelectric made product.

2.2 Ferroelectric Properties

Over the last 10 years, there were considerable studies properties of ferroelectric materials and devices. Ferroelectrics are the interesting polar materials that exhibited properties at least two equilibrium orientations of the spontaneous polarization vector in the application of an external electric field, and in which the spontaneous polarization vector may be switched between those orientations by an electric field [Lines M E and Glass A M, (1979)] . This effect occurred by separation of the center in positive and negative electric charge, making one side of the crystal positive and another side negative. These charges can be reversed by the application of electric field. Most ferroelectric materials undergo a structural phase transition from a high-temperature para-electric phase into a low-temperature ferroelectric phase (see Figure 2.1).

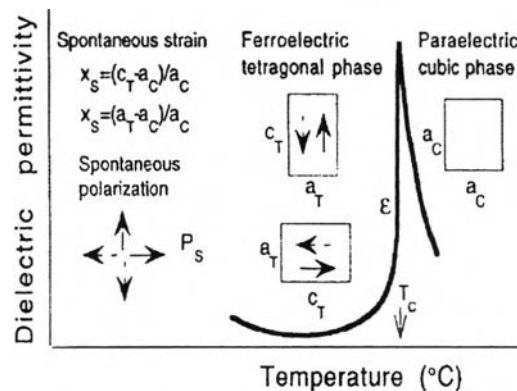


Figure 2.1 The changes in a ferroelectric material that transforms from a paraelectric cubic into ferroelectric tetragonal phase with temperature.

2.2.1 Ferroelectric Hysteresis Loop and Polarization Switching

The most important characteristic of ferroelectric materials is polarization reversal (switching) by an electric field. The result of the domain-wall switching is occurred by the ferroelectric hysteresis loop (Figure 2.2) that can be experimentally observed at small values of the AC electric field, the polarization increases linearly with the field amplitude. When the field is increased, the polarization will start to

switch (segment BC) until all the domains are aligned in the field direction (C point), then ferroelectricity is linear (segment CD). If the field strength was decrease, domains will back-switch, but at zero field (no applied field), the polarization is non-zero (point E), so-called the remanent polarization (P_R). To reach a zero polarization state the field will be reversed (point F). Further increase of the field in the opposite direction will cause a new alignment of dipoles and saturation (point G). The field strength is called the coercive field (E_C) that necessary to bring the polarization to zero and reversed to complete the cycle. An ideal hysteresis loop is symmetric which $+E_C = -E_C$ and $+P_R = -P_R$ [Haun M J, Zhuang Z Q, *et al.*, (1989)]. The ferroelectric property can be classified into piezoelectric materials and a subset of piezoelectricity is pyroelectricity, whereas the polarization is the function of temperature.

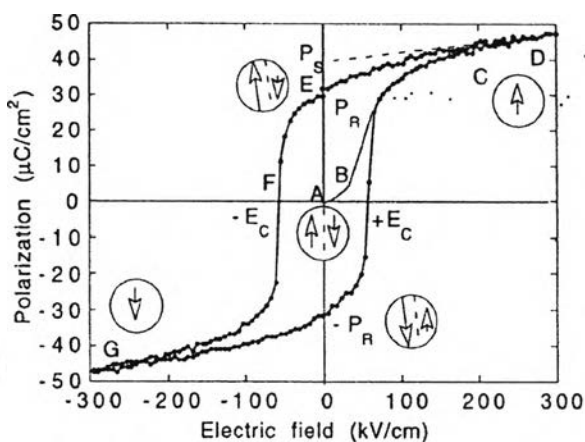


Figure 2.2 Ferroelectric P - E hysteresis loop. Circles with arrows represent the polarization state of the material at the indicated fields.

Not all piezoelectricity are ferroelectrics as shown in Figure 2.3 by classification of element crystals into 7 systems such as triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal and cubic. All of these can be divided by symmetry elements into 32 groups.

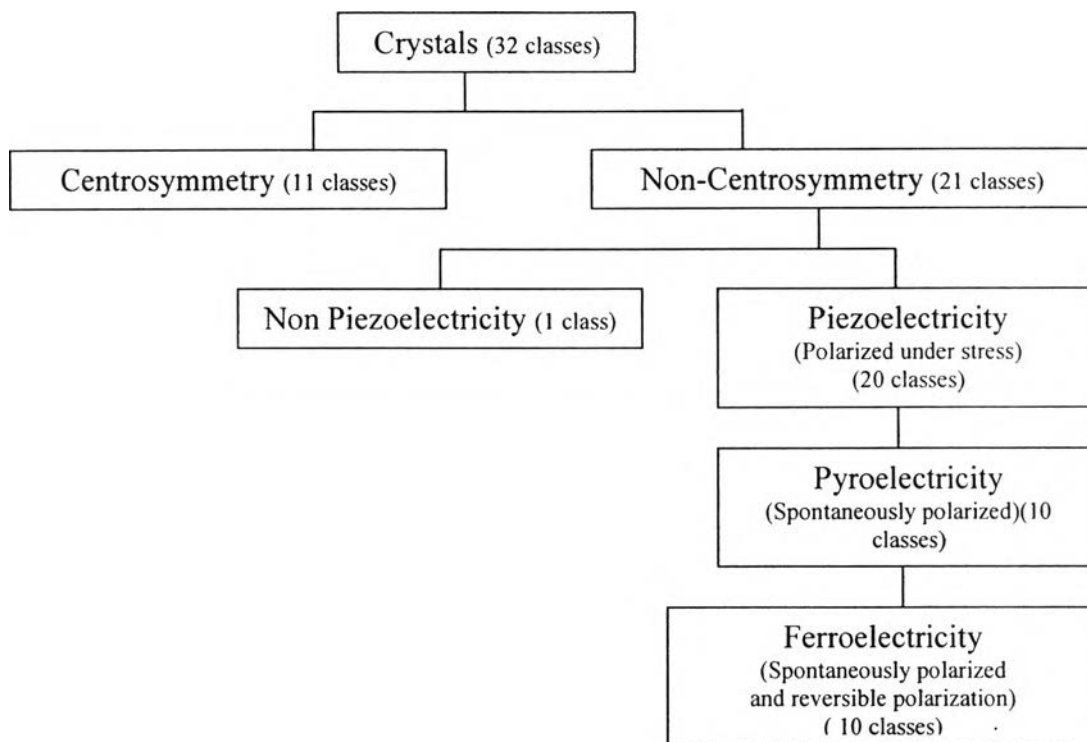


Figure 2.3 The system of crystals in 32 classes.

2.3 Piezoelectric Properties

The word “Piezo” is derived from the Greek “piezein”, meaning to press tight or squeeze, describes piezoelectric as “pressure electricity”. The piezoelectric effect was discovered in 1880 by the Jacques and Pierre Curie. They found that when a mechanical stress was applied on a crystal (when piezoelectric materials were mechanically deformed), they generate an electric charge. Conversely, when an external electric field is applied to piezo-electric materials they are mechanically deformed [Walter G. Cady (1964)].

2.3.1 The Concept of Piezoelectric

Piezoelectric crystals are showed in two effects. First, the direct effect (designated as a generator) is identified with the phenomenon whereby electrical charge (polarization) is generated from a mechanical stress, whereas the converse effect (designated as a motor) is associated with the mechanical movement generated

by the application of an electrical field. Both of these effects are illustrated in Figure 2.4 [Gene H. Haertling (1999)].

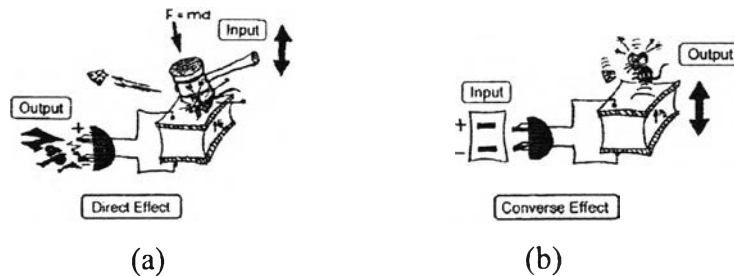


Figure 2.4 The effect of piezoelectric material (a) direct piezoelectric effect (b) converse piezoelectric effect.

The basic equations that describe these two effects in electric and elastic properties are:

$$D = d \cdot T + \epsilon^T \cdot E \quad \text{direct effect} \quad (4)$$

$$S = s^E \cdot T + d^T \cdot E \quad \text{converse effect} \quad (5)$$

Where D is the dielectric displacement, T is the stress, E is the electric field, S is the strain, d is a piezoelectric coefficient, s is the material compliance and ϵ is the dielectric constant (permittivity). The superscripts indicate a quantity held constant: in the case of ϵ^T , the stress is constant, which means that the piezoelectric element is mechanically unconstrained, same as s^E , the electric field is constant, which means the electrodes on the element are shorted together.

2.3.2 Piezoelectric Coefficients

According to isolation of force or poling vectors to single mode, the relationship between charge density and applied force was known as piezo-strain constant (d_{ij}), specified with subscripts to identify the conditions which determined for example; d_{31} indicates that this piezoelectric coefficient relates to the generation of polarization (direct effect) in the electrodes perpendicular to the 3 or vertical direction and to the stress mechanically applied in the 1 or lateral direction; d_{33} indicates

the polarization generated in the 3 direction when the stress is applied in the 3 direction (Figure 2.5).

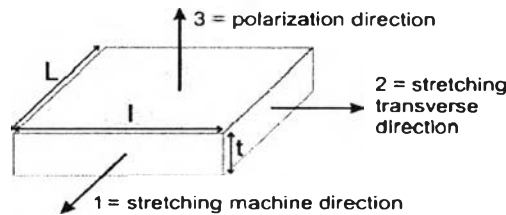


Figure 2.5 Specific direction and axis of piezoelectric.

In concept of piezoelectric effect, it can be described by four piezoelectric coefficients such as d_{ij} , e_{ij} , g_{ij} and h_{ij} which are related the electrical characteristics such as the electric induction D and the electric field strength E , and the mechanical parameters such as the mechanical stress X and the strain x (Figure 2.6).

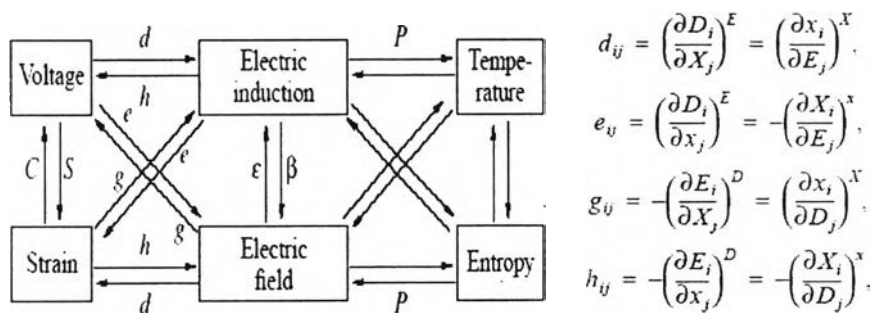


Figure 2.6 Schematic diagram of the relation of the electromechanical coefficients for piezoelectric and pyroelectric materials.

The subscripts are: $i = 1-3$ and $j = 1-6$. The superscripts refer to the experimental conditions: E indicates zero electric field (a closed circuit), D corresponds to zero electric induction (an open circuit), X stands for zero mechanical stress (a free sample), and x denotes zero strain (a fixed sample) [V. V. Kochervinskiĭ. (2003)].

2.3.3 Piezoelectric Applications

For many years, there are many applications of piezoelectric materials not only ceramic materials but also are the piezo-plastic materials which defined for polycrystalline materials, or at least in the crystalline region of semi-crystalline materials [Harrison, J.S (2001)]. The requirement for flexible and large area piezoelectric materials for many applications was recognized. Because ceramic is fragile, environmental hazards, and difficult to produce a large size by a complex fabrication routes. Polymers are more interesting as a new piezo-electric material than ceramic. The discovery of piezoelectricity that has a largest progress in this field was made by Poly(vinylidene Fluoride) or (PVDF) that leading to piezoelectric polymers .

The applications of PVDF was reported by several investigators, such as sensor, ultrasonic, acoustic microscopy transducer, micro-electro-mechanical devices (MEMS), medical ultrasonic imaging [Yoseph Bar-Cohen *et al.*, (1996)] [Smolorz, and Grill, (1995)] [Harsanji, (1995)]. Due to PVDF shows a strong piezoelectric response even at microwave frequencies, little resonant background noise (clarity of signal), allows to fabricate in a wide variety shapes for special applications and low acoustic impedance (close to that of water) toughness and chemical inertness and also, the PVDF film show pyroelectric effect. This response makes it an excellent sensor for infrared (heat) detection of the human body. This research will be focus on PVDF materials, owing to their higher piezoelectric coefficient than those of other polymer.

2.4 Poly(vinylidene fluoride) (PVDF)

The discovery of piezoelectric in PVDF by Kawai in 1969 has attracted much attention to this polymer. They found that the poly(vinylidene fluoride) exhibited large piezoelectric effect after poling. Due to PVDF has a $-(\text{CH}_2\text{-CF}_2)_n-$ repeat unit occupies a half-way point in the homologous series of fluorinated vinyl monomers stretching from polyethylene (PE) to poly(tetrafluoroethylene) (PTFE). The PVDF is typically 50–70% crystalline with at least four different crystals including form II (α -phase), form I (β -phase), form III (γ -phase) and form IV (δ -phase), which could transform from one to the other under certain conditions.

The common polymorph of PVDF was α (TG^+TG^-) conformation, which could be produced during crystallization from the melt. The most important polymorph with outstanding piezoelectric and pyroelectric properties is β form that has a TTT conformation (all-trans) as show in Figure 2.7. The γ form has a GTTT conformation while δ corresponds to the polar form of α .

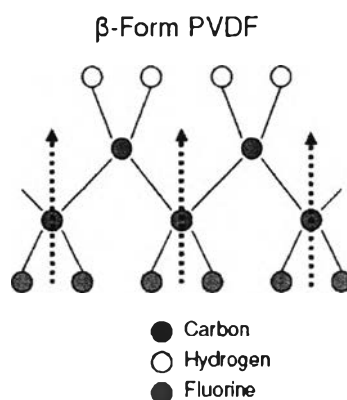


Figure 2.7 The β form of PVDF

When PVDF is in β form structure, the dipole is strongest. This structure aligns all of dipoles throughout the polymer chain creating polarization that extends to the boundaries of the PVDF. These dipoles are allowing PVDF to act as a sensor or transducer. The β crystal in PVDF could be obtained from a modification by various processes such as mechanical deformation, poling under large electric fields, crystallization from the melt under high pressure very high cooling rates [Nalwa, Hari Singh, (1995)].

Different methods for generation of the β conformation from the melt or from other PVDF conformations are shown in Figure 2.8.

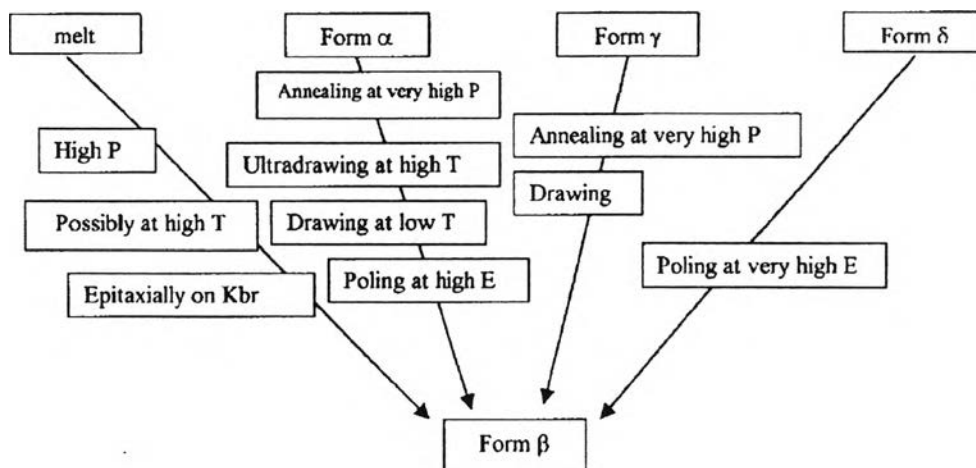


Figure 2.8 Transitions from different conformations of PVDF to β -phase.

2.4.1 Preparation of Piezoelectric PVDF Film

PVDF film can be manufactured by solidification of the film, produced by film extrusion, compression molding, solvent casting and etc., from a molten phase. In this research, solvent-casting solution method will be employed for producing PVDF film. Lovinger (1982) developed a very helpful diagram (see Figure 2.9), which indicates the various solvent, such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and monochlorobenzene (MCB), which along with cyclohexanone are solvents which are used for solvent casting in which the different phase conformational changes and phase transformation mechanisms can be prepared, to produce PVDF films.

The variations of solvent polarity and temperature induced a specific conformation in PVDF chains, through the changes in chain coil dimensions and important in stabilizing conformations of PVDF in crystalline phases. Experiments by Salimi, A., Yousefi, A.A., (2004) show that there was no change on the solution-crystallized film in cyclohexanone (weak-solvent) in the temperature range of 50-120 °C. On the other hand, DMAc (good-solvent) solution-crystallized films, crystallization mainly results in formation of trans states (β -phases) at low temperature, whereas at higher temperatures gauche states become more populated (α -phase) [Salimi, A., Yousefi, A.A., (2004)]. As mention earlier, this observation is common to both β -phase (I) and γ -phase (III) but is very strong

tion is common to both β -phase (I) and γ -phase (III) but is very strong piezoelectric coefficient only in form I.

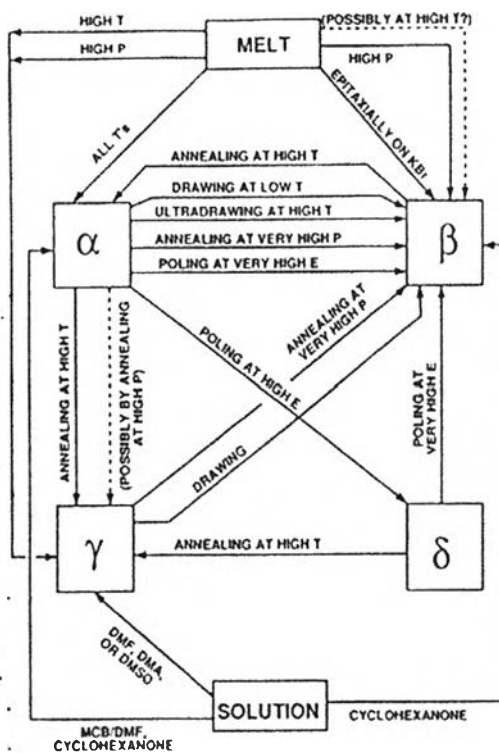


Figure 2.9 The interrelations among the four well-established phases of PVDF [A. J. Lovinger, (1982)].

In solidifications of PVDF film, Chun-Hun Du, *et al.*, (2006) that observed the vibration bands of FTIR at 530, 615, 766, 795, 855, 976, 1214 and 1383 cm^{-1} referred to the α phase while the bands at 470, 510, 600, 840, 1279 and 1431 cm^{-1} corresponded to the β -phase. It was observed that the quenching temperature of PVDF film was below 30 $^{\circ}\text{C}$ and the samples of PVDF-HFP exhibited mainly the β -phase. When the quenching temperature was increased, the β -phase was almost disappeared and α -phase characteristic band was mainly exhibited. Also, if the critical quenching temperature of pure PVDF was near 40 $^{\circ}\text{C}$, relative content of the β -phase was higher than that of the α -phase when the film thickness was below 8 μm , this was present in Figure 2.10.

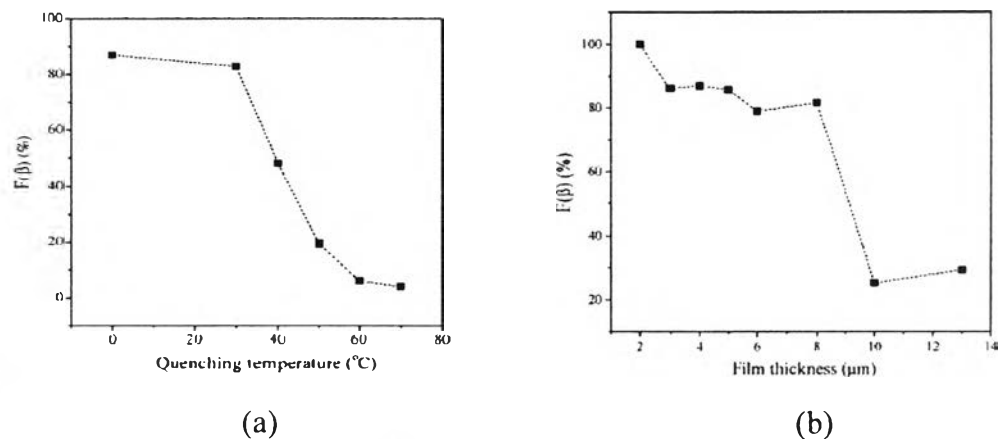


Figure 2.10 Dependence of relative amount of β -phase, $F(\beta)$, on (a) quenching temperatures and (b) Film thickness.

Unfortunately, α -phase is thermodynamically more stable in PVDF than β - phase and it is difficult to obtain a β -phase dominant PVDF thin film on a substrate. Applying a mechanical stretching process in bulk PVDF film can produce more β - phase than α -phase.

2.4.1.1 Stretching of PVDF film

The β/α ratio of stretched PVDF film were affected by stretching of temperature, rate, and ratio [Chun-hui Du, *et al.*, (2006)]. The influence of stretching temperature was revealed when stretched near 70°C , α -phase to β -phase transformation was sufficiently high. If stretching above 80°C result in a lower α to β phase transformation. At 140°C , the chain mobility's are higher, resulting in re-crystallization to α form. When stretched at 150°C show that the γ to β transformation will occur [Servet, D.Broussoux, (1981)]. Then P. Sajkiewicz, *et al.*, (1999) suggested that the abrupt change of orientation of β crystallites occurred in the range between 70 and 87°C . The explanations on α to β phase transformation were described by the α_c (transition/relaxation), which was associated with the molecular motions in the crystalline/amorphous inter-phase.

Other factors that increased the β/α ratio of PVDF film are stretching rate and ratio of stretching. Matsushige, K. *et al.*, (1980) observed that PVDF

sample necked upon stretching at room temperature and α to β phase transformation at the necked region by WAXD. While, uniaxial stretching greatly enhances piezoelectric properties of the film. This way due to stretching enhanced the β phase transformation which orients the polymer chains in a specific direction (Figure 2.11).

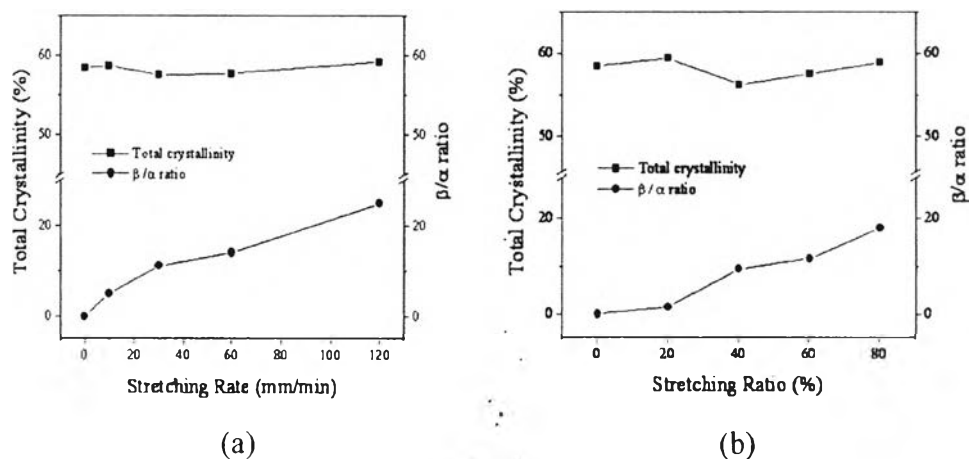


Figure 2.11 The effect of stretching rate (a) and ratio (b) in β / α ratio.

Stretching also influenced piezoelectric properties of PVDF thin films, due to orientation of β -phase crystal, which provided uniform lattice dipole moments of crystals [Mohammadi, B, *et al.*, (2007)]. Uniaxially and biaxially effect were studied by Naarayan, S.S., *et al.*, (2005). They show that the piezoelectric constants increased in the longitudinal direction with increasing superimposed strains and decreased in the transverse direction for uniaxially stretched PVDF. So, without drawing, PVDF shows a very weak piezoelectric behavior. Jerry Scheinbeim, *et al.*, (1996) found that doping with tricresyl phosphate (TCP) enhanced the piezoelectric activity, the pyroelectric coefficient, and the remanent polarization, while stabilizing the remanent polarization to higher temperatures. But α to β crystal phase transformation is not as complete, due to the internal lubrication.

Although β -form was occurred in PVDF film, the dipole moments of PVDF film are randomly oriented resulted in no net dipole. Also the highest piezoelectricity was obtained from certain poling conditions.

2.4.1.2 Poling of PVDF film

A second step, when an electric field was applied under PVDF film, it is known as poling. Polymer chains inside the crystallites align themselves along the field by rotating the dipoles around the chain axis. Marta M.D. Ramos, *et al.*, (2005) showed that poling had two main effects at a structural level, the reorientation of the dipoles along the field direction and the transformation from the α -to the β -phase. These poling effects are presented in Figure 2.12, the α to β transformation is optimized by the poling process indicate from the decreasing of the absorbance of the 615 cm^{-1} and 763 cm^{-1} modes. When an electric field of 50 MV/cm , or greater strength, is applied to the stretched chain perpendicular to the chain axis, a rotation of $-\text{CF}_2$ and $-\text{CH}_2$ around the chain axis in the opposite directions was predicted. Effect of high applied electric fields (100 MV/cm) on a PVDF chains was also been investigated. Results suggested that such high electric field could cause direct transformation from α to β conformation.

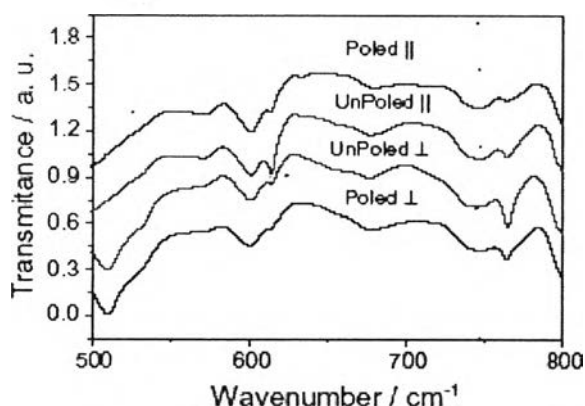


Figure 2.12 FTIR spectra of poled and non-poled samples of β -PVDF 500 cm^{-1} to 800 cm^{-1} region.

The poling fields and times were found to play important role in the crystallization as well as the piezoelectric activity of PVDF film [T.T. Wang and J.E. West, (1982)]. Figure 2.13, the poled polymer exhibited the XRD peaks corresponding to the reflection from the (110) and (200) planes in the β -phase structure.

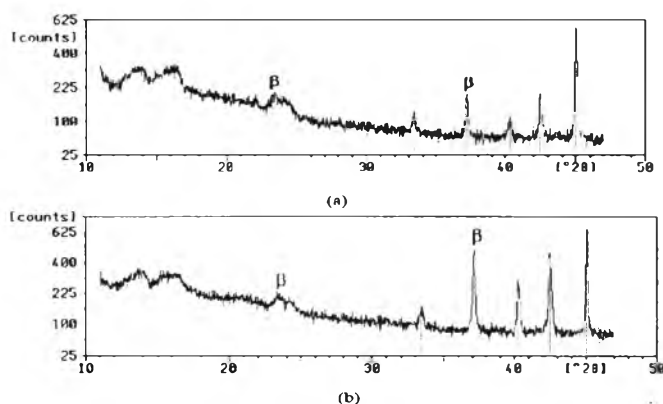


Figure 2.13 XRD pattern of tape cast PVDF sample with a poling field of (a) 300 MV/m and (b) 400 MV/m.

The ferroelectric properties of PVDF film are related to the polarized crystalline phase, which coercive field, spontaneous and remanent polarization and shape of the loop may be affected by many factors such as the thickness of the film, the presence of charged defects, mechanical stresses, preparation conditions, and thermal treatment [Haun M J, Zhuang Z Q, *et al.*, (1989)].

At high electric fields, polarization occurs in semicrystalline polymers. This nonlinearity in polarization is defined as hysteresis, two properties typically reported for ferroelectric materials are the coercive field and the remanent polarization. PVDF demonstrates hysteresis loops similar to those known from crystalline ferroelectric materials [Wang, Herbert and Glass (1988)].

The change in the D–E loops after short term (48 h) thermal annealing of a homo PVDF polymer was presented by Mathew Celina, *et al.* (2005) in Figure 2.14. As the annealing temperature is increased the remanent polarization (P at $E = 0$) decreases due to thermal de-poling.

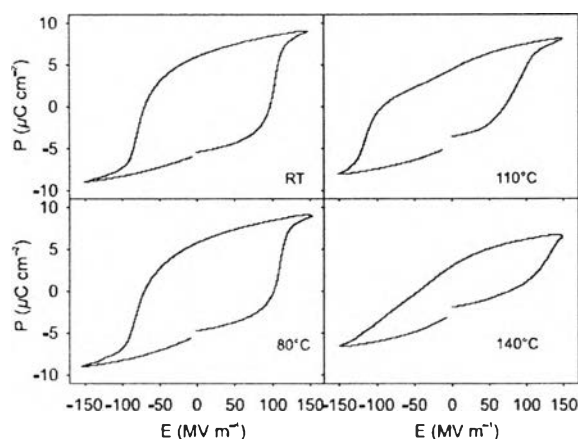


Figure 2.14 Loss of polarization potential in a homo PVDF polymer after annealing.

This polarization of PVDF film remains constant for many years, if it is not influenced by the effects of moisture uptake or elevated temperature. Because of polymers also typically possess a high dielectric breakdown and high operating field strength, which means that they can withstand much higher driving fields than ceramics. It can be noted that ferroelectric PVDF is not suitable as dielectric for capacitors in applications of high field AC or high field DC at fast repetition rates [T. R. Jaw and P. J. Cygan, (1993)]. Thus, the β -PVDF chains have a net dipole moment, pointing from the electronegative fluorine to the electropositive hydrogen, producing a net dipole moment nearly perpendicular to the polymer chains which these material behave like a piezoelectric materials.

In Table 1, piezoelectric polymers have much higher piezoelectric stress constants (g_{31}) indicating that they are much better sensors than ceramics. Other features of polymers are low elastic stiffness, and low density which result in a high voltage sensitivity (excellent sensor characteristic), and low acoustic and mechanical impedance (crucial for medical and underwater applications). In spite of the d_{33} , d_{31} piezoelectric coefficients, dielectric constant was lower than ceramic. Judovits, L. (2006) studies on thermal analysis of poly(vinylidene fluoride) film, showed that the unconstrained film leads to the melting properties of a relaxed material and the relaxation that took place upon heating seemed to have reorganization response.

Table 2.1 Comparison between the properties of PVDF and some common piezo-electric ceramic material [Justin E. George (2007)]

Properties	PVDF film	PZT	Units
Density	1.78	7.5	10^3 kg/m^3
d_{31} Constant	23	110	10^{-12} C/N
d_{33} Constant	-23	593	10^{-12} C/N
k_{31} Constant	12	30	% at 1 KHz
g_{31} Constant	216	10	10^{-3} Vm/N
Young's modulus	4-6	71	GPa
Acoustic Impedance	2.7	30	$10^6 \text{ kg/ m}^2\text{-sec.}$

Due to the comparison of PVDF and ceramic, many researchers have put efforts to improve the properties of PVDF to be used substituently such as the making of PVDF co-polymers, including P(VDF-TrFE) and P(VDF-TeFE) and others to improve the properties of PVDF [Bar-Cohen, Y., (1996)]. The composites of PVDF/ $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ by 0-3 connectivity at various amount of ceramic powders in composites was found the increasing in dielectric constant and piezoelectric properties of composites [Kittikun *et al.*, (2007)]. Following, the polymer foam electrets (ferroelectrets) resemble close similarities to ferroelectrics, were shown a large intrinsic piezoelectric d_{33} -coefficients higher than 100 pC/N [Bauer, Siegfried *et al.*, (2006)]. Similarly, Neugschwandtner *et al.*, (2001) shown the charges generated during the plasma discharge are trapped in surface states (Figure 2.15), resulting material which carries positive and negative charges on the internal void surfaces, is called a ferroelectret. Also, the response for the large piezoelectric effect and a quasi-static piezoelectric d_{33} coefficient was about 250 pC/N and a dynamic d_{33} coefficient of 140 pC/N at 600 kHz, hence they provide a novel class of ferroelectric materials. On the other hand, it has a limited thermal stability up to 50 °C in the polypro-

pylene material. At about the same time, commercial as well as experimental films of porous polytetrafluoroethylene (PTFE) became available. An experimental porous PTFE material proved to possess a good electret properties with this material, quasi-static piezoelectric coefficients of < 35 and 150 pC/N were reported on single films of porous PTFE [Michael *et al.*, (2005)].

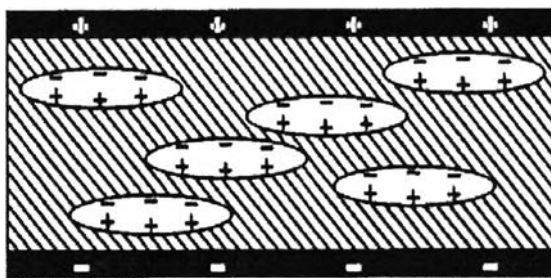


Figure 2.15 Schematic sketch of a charged polypropylene foam electret, the charged voids form perfectly oriented macroscopic dipoles responsible for pyro- and piezoelectricity.

From previous works mentioned above, space-charge polymers may become candidates for successful ferroelectret film but not many researchers mentioned a PVDF space-charge. This research is interested in porous or space-charge; new concept will be apply to overcome the problems of PVDF film which is expected to have high piezoelectric coefficient, and less relaxation.

2.5 Porous Poly(vinylidene fluoride) Film

2.5.1 Film Membrane

Nonporous membranes, isotropic microporous membranes, electrically charged membranes and asymmetric membranes can be classified in four types of membrane. In present work, the isotropic microporous and asymmetric membrane to study a new concept of a space charges was emphasized (Figure 2.16). Isotropic microporous has a highly voided structure with randomly distributed, interconnected pored. Usually, the pores are extremely small, in the diameter range of $0.1-10 \mu\text{m}$

that widely used in microfiltration and ultrafiltration. On the other hand asymmetric membrane have an extremely thin surface layer supported on a much thicker porous substructure and defect-free films to about 20 μm thickness [Howe-Grant, M, (1993), R. W. Baker, (2004)].

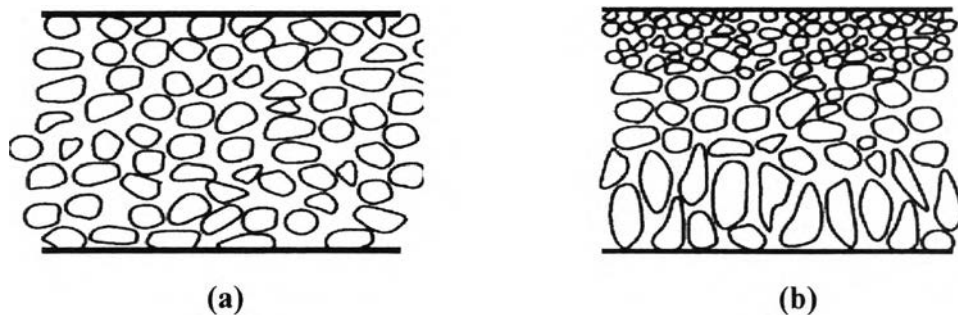


Figure 2.16 The structure of (a) Isotropic microporous membrane (b) Asymmetric membrane.

2.5.2 Preparation of Porous PVDF Film

2.5.2.1. *Phase Inversion Technique*

The main techniques usually exploited for preparation of porous PVDF film are irradiation, expanded film, template leaching and solution precipitation to produce a porous PVDF film. In addition, each process gives different membrane characteristics e.g. average pore size, porosity, mechanical properties, and even selectivity. The first three methods gave isotropic microporous membranes while the last one produces asymmetric microporous membranes [Howe-Grant, M, (1993)].

Usually, the membranes are prepared by using the solution precipitation or phase inversion. In this method, the polymer precipitation can be induced by several ways such as cooling, solvent evaporation and immersion in non solvent. In immersion technique by using non solvent, a polymeric casting dope is immersed in a non solvent bath to induce precipitated, when the diluents are subjected to a temperature below the equilibrium melting temperature of the polymer solution, the system undergoes S–L separation via polymer crystallization. During the crystallization process, the diluents are rejected to the inter-spherulitic regions. Upon diluents ex-

traction, the inter-spherulitic regions, diluents-rich regions, become the membrane pores.

The variations of membranes with cellular, spongy, spherulitic structures and porosity properties of the PVDF membranes are controlled by varying on the casting and immersion parameters such as dope, bath compositions, precipitation temperature, additives, etc.

A. Effect of PVDF concentration

Figure 2.17 shows a smaller average pore radius and porosity influenced by casting solutions with a higher polymer concentration, while the membranes with larger average pore radius and higher porosity were fabricated from a lower polymer concentration [M. Tomaszewska, (1996), C. Feng *et al.*, (2004)].

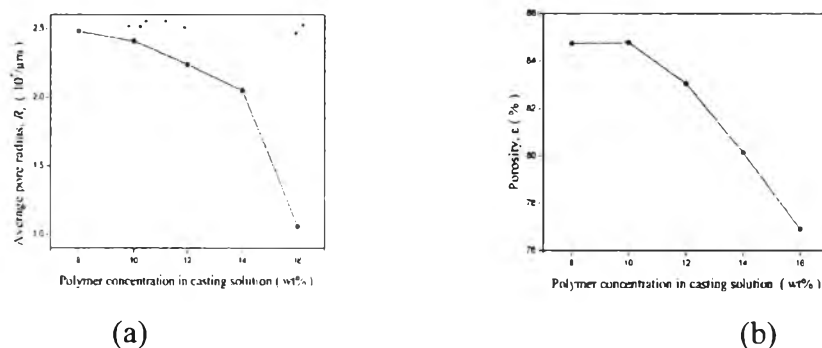


Figure 2.17 Concentration in casting solution on (a) average pore radius and (b) porosity of the resultant membrane.

B. Effect of solvent

Following, M. L. Yeow, (2003) show the rank solvent power was revealed that $\text{DMAc} > \text{NMP} > \text{DMF} > \text{TEP}$, The stronger the solvent power, the greater the amount of nonsolvent (in this case water) that is required to disturb the system equilibrium and induce the polymer precipitation The value of porosity was studied by Minghao Gu (2006), shown porosity of PVDF film decreased as the interactions increased. Bottino *et al.* were studied the PVDF phase-inversion by changing experimental parameters, which can obtain two different morphologies such as sponge-like

and finger-like by various the solvents as shown in Figure 2.18 [E. Quartarone, (2002)].

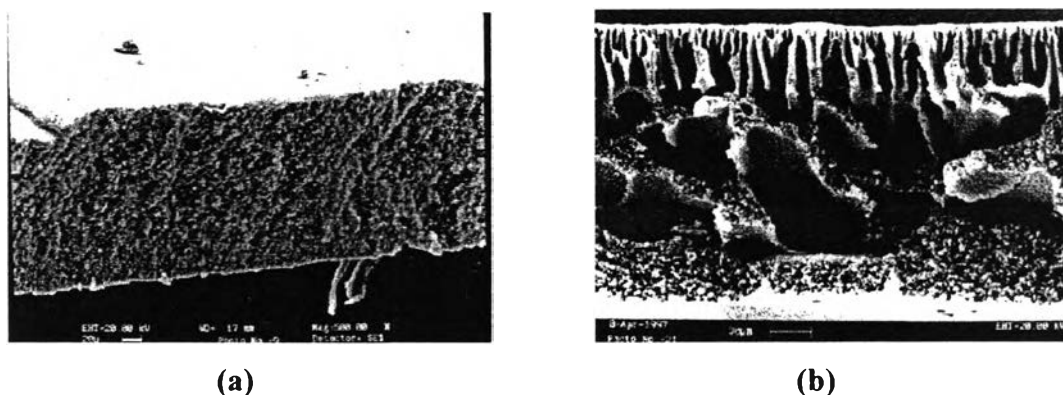


Figure 2.18 SEM micrographs of two high porous (~75 vol %) PVDF homopolymer membranes in (a) a sponge-like and (b) a finger-like texture.

C. Effect of quenching conditions and temperatures

The spherulite growth rate of PVDF was high at elevated temperature, as droplets had more time to congregate, while the structure and size of pores was unvaried as coarsening or quenching depth increased [Minghao Gu, (2006)]. Liao-Ping Cheng, (1999) carried out experiments at three different temperatures 25, 45, and 65 °C, when PVDF was precipitated at higher temperatures (65°C) from 1-octanol/DMF, was obtained largely in the α -form (type II) crystal structure.

D. Effect of coagulation temperature

An increasing in the coagulation temperature seems to have an influence on the coagulation rate for PVDF systems. The continual decreased of average pore size and porosity was observed with increasing temperature of precipitation bath [C. Feng *et al.*(2004)].

Other method that can provided a porous films such as a spin coated technique [Min Soo Park *et al.*, (2006)], the CAB solutions was mixed with THF/chloroform under humid Condition about 95%, were spin-coated on silicon wafer substrate at 1000 rpm. A water-miscible solvent under humid conditions have in-

fluence of porous effect. Also, high to low polymer concentrations, various porous morphologies are generated: (i) an asymmetric porous structure where the top layer has many pores while a few pores with small size are observed inside the film, (ii) a porous structure in which pores can be seen in entire film thickness, (iii) a symmetric two layered porous structure, and (iv) a one layer porous structure. Another method that β -PVDF film were irradiated by ion beam of Sn. The solution of KOH 9 mol L⁻¹ and saturated in KMnO₄ was the best etching reactant for PVDF so-called “chemical etching dealing”, pore diameters of this method less than 1 μ m. The spectroscopic data reveals that the formation of pores occurs by a two-step mechanism: (i) double bonds as a result of dehydrofluorination induced by alkaline media and (ii) oxidation of these double bonds in permanganate solution [M. Grasselli, N. Betz, (2005)].

2.5.2.2. Compression Molding Technique

The second method is blowing agent technique; this technique polymer is mixed with blowing agent which generates a gas during the period when the polymer is beginning to solidify. The polymer heat and compress in mold. Blowing agents, also called foaming agents, can be classified as Physical and Chemical Blowing Agents. Physical blowing agents are not under chemical changes during processing. Physical blowing agents are in forms of liquid or compressed gas which will transfer state into gases or low boiling liquid during processing causing resins into cellular structure. Chemical Blowing Agents are mainly solid form of hydrazine derivatives include Azodicarbonamide; p,p'-Oxybis(benzenesulfonyl hydrazide); 5-Phenyltetrazole; p-Toluene sulfonyl semicarbazide; Trihydrazine Triazine; They commonly release gases such as nitrogen, carbon dioxide, carbon monoxide or ammonia. But ammonia is not desirable as it effects on degrade of resins. There are non-azo blowing agents releasing carbon dioxide such as sodium borohydride. [J. Murphy (2001)].

In this research use Azodicarbonamide (AZDC, ADCA, AZDN) as a chemical blowing agent which has a decomposition temperature of 210-230 °C.

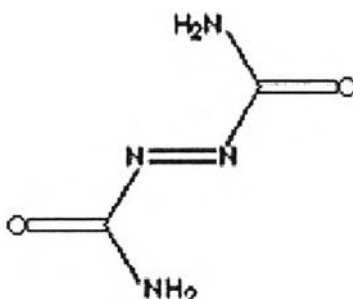


Figure 2.19 The chemical structure of Azodicarbonamide.

Aliphatic azo compounds are unstable and the loss of nitrogen gas occurs by the simultaneous cleavage of carbon-nitrogen bonds, resulting in carbon-centered radicals. Some aliphatic azo compounds are utilized as radical initiators. Azodicarbonamide, releasing nitrogen gas, is a general foaming agent for rubbers and plastics such as PVC, EVA, polyolefin, polystyrene products. (Its temperature of decomposition is 205 - 215 C). It is also used as an aging and bleaching ingredient in cereal flours and dough conditioner in baking bread. Azodicarbonamide acts as a hydrogen acceptor, converting to biurea.

In this research, the morphology, pore structure, mechanical strength, dielectric constant, dielectric loss, and piezoelectric coefficient of homo-PVDF porous film which fabricated in 2 methods are phase inversion and blowing agent technique will be examined.