



CHAPTER II

LITERATURE REVIEW

2.1 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 2.1. The γ form has a GTTT conformation while δ corresponds to the polar form of α .

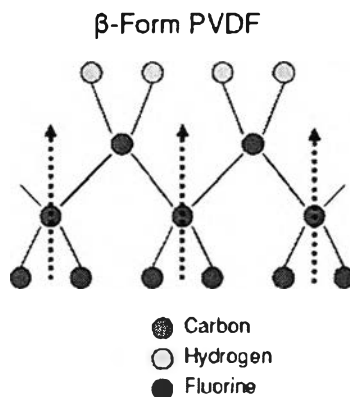


Figure 2.1 The β form of PVDF

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, 1995).

Different methods for generation of the β conformation from the melt or from other PVDF conformations are shown in Figure 2.2.

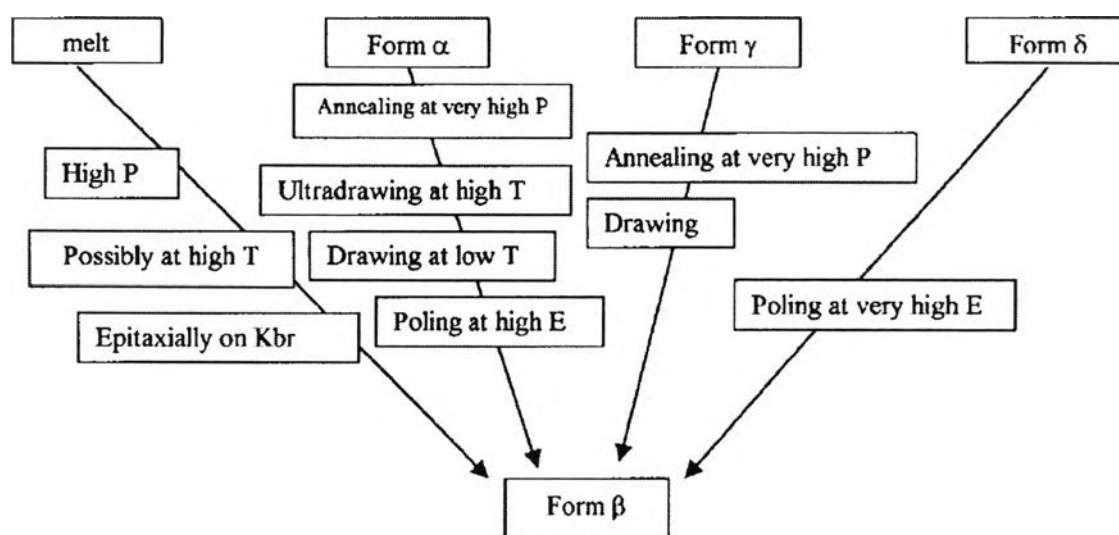


Figure 2.2 Transitions from different conformations of PVDF to β -phase.

2.2 Barium Strontium Titanate (BST) Ceramic

Ferroelectric materials are very promising materials for a wide range of applications. As they present non-linear variation of dielectric constant with the electric field, high dielectric constant and moderate loss in microwave domain, ferroelectric materials present also a high potential for microwave applications [Fiedziuszko *et al.*, 2002., Kozyrev *et al.*, 2000]. Barium strontium titanate (BST) is an insulating material with large relative dielectric permittivity and small dielectric loss near ambient temperature [Ezhilvalavan *et al.*, 2000]. It has been regarded as one of the most promising ferroelectric materials, finding applications in capacitors,

actuators and sensors for energy storage and conversion, automatic control, acoustic and pressure transducers, detectors, optical modulators and many other electronic devices [Agarwal *et al.*, 2002., Biesheuvel *et al.*, 1999]. BST can be easily prepared by substitute Sr^{2+} ion for TiO^{2+} and Ba^{2+} ion of BaTiO_3 in the ion lattice via sol-gel method. Jeon (2004) studied effect of SrTiO_3 on dielectric constant, he found that the peak value of dielectric constant at the Curie temperature of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics was found to be dependent on SrTiO_3 concentration and maximum dielectric constant of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics at curie temperature increased with an increase in the x value and sintering temperature.

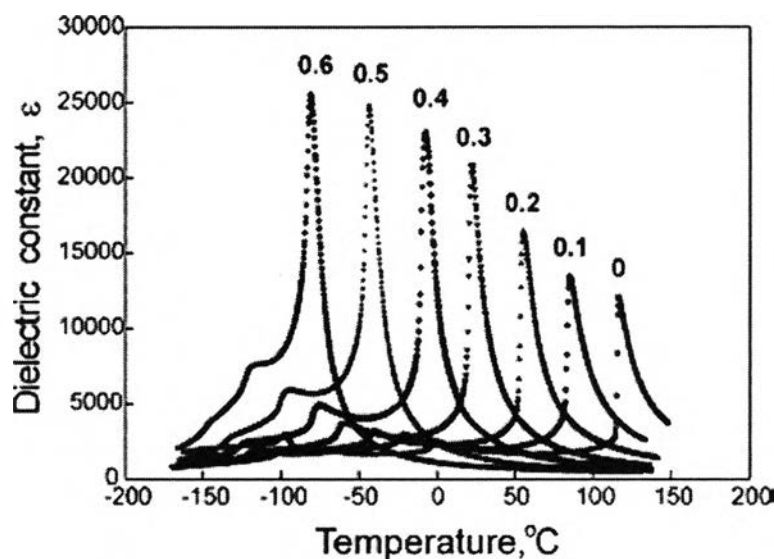


Figure 2.3 Dielectric property of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics sintered at 1450°C for 1 h.

However, the suitable composition which could be used in any room temperature application was $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ with $x=3$ because at this composition, ceramic yielded highest dielectric constant at curie temperature near room temperature as shown in Figure 2.3.

2.3 Piezoelectric Composite

Ferroelectric ceramic/polymer composites consisting of ferroelectric ceramic powder embedded in a polymer matrix have attracted much attention since they combine the excellent ferroelectric properties of the ceramics and the flexible mechanical properties of the polymer [Das-Gupta *et al.*, 1989]. For the film mechanical application, homogeneity of composite films was necessary to use ceramic powder with both suitable dielectric property and sizes significantly smaller than the thickness of the film. Thus ceramic powder with particle sizes in the nanometer range can be aspired. The sol-gel method has recently been intensified because the particle size of the ceramic powder can be not only up to nano-meter but also dispersed uniformly. But it is still possible to form inhomogeneous ceramic/polymer composite thin films because nano-meter particles are easily to accumulate together [Dong *et al.*, 2004]. Kohpaiboon and coworker studied composite film of PVDF and BST, they found much increasing of dielectric constant at all frequencies. And also the value increased with the BST ceramic content.

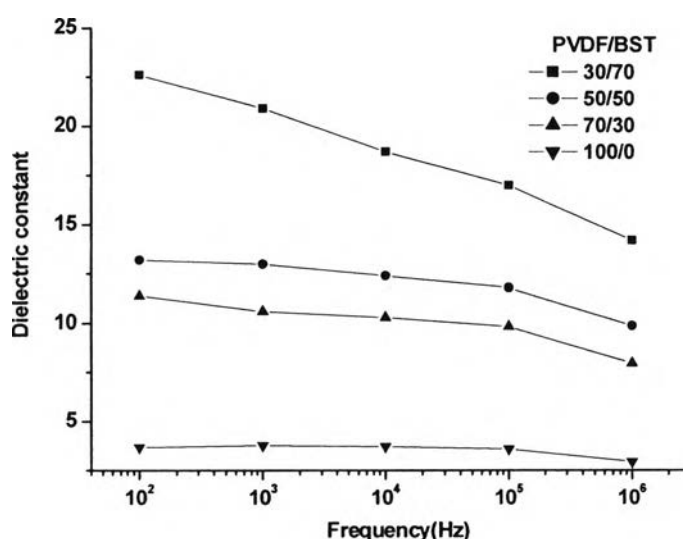


Figure 2.4 The frequency dependence of the dielectric constant of PVDF/calcined $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ at 800°C composites in weight proportions of 100/0, 70/30, 50/50 and 30/70.

2.4 Laminated Poly(vinylidene fluoride) Film

Wada, (1987) divided the piezoelectricity of polymeric systems into five classes: (I) Polypeptide type, or more generally, uniaxially oriented systems of optically active polymers, (II) PVC type, or in general, polar polymers such as polyvinylchloride (PVC) and polyvinylfluoride (PVF) with frozen dipole orientation, (III) Ferroelectric polymers such as polyvinylidene fluoride (PVDF), (IV) Dispersed composite in which fine particles of ferroelectric ceramics are dispersed in a polymer matrix, and (V) Multilayer composite in which one of the layers is an electret. All of these materials except (I) possess spontaneous polarization and thus also exhibit pyroelectricity. A multilayer system in which one of the layers is an electret shows piezo- and pyroelectricity. A general theory of these activities has been developed by Hayakawa and Wada [Mort *et al.*, 1982].

The nature of piezoelectricity of multilayered polymer system depends on the physical and chemical properties of their components. Most heterogeneous polymer films can have piezoelectric properties to some degree, even if they are not polarized [Greaves *et al.*, 1974, Hayakawa *et al.*, 1973, Wada *et al.*, 1976]. This may be related to heterogeneity and embedded charges accidentally present in the film. Uncharged laminate PET-PMMA/BaTiO₃-PET exhibits piezoelectric properties. This laminated system of three-layered structure of different materials fulfills the heterogeneity condition, moreover the charges can be stored at the interfaces of the layers as a result of the equilibrium triboelectric electrification and some effects caused by partially-oriented PET films. However, PMMA/BaTiO₃ composite was used as an internal layer of the laminate shows interesting piezoelectricity to some extent due to the spontaneous polarization of barium titanate particles, and the dipole polarization of PMMA [Mazur, 1989]. Similar piezoelectric laminates have been prepared by using polyester-urethane elastomer (PUE) and PMMA/PUE as an internal layer of the PET-PUE-PET and PET-PMMA/PUE-PET systems. These laminates, both uncharged and charged by an external electric field at higher temperature, can have interesting electret and piezoelectric properties [Mazur, 1990].

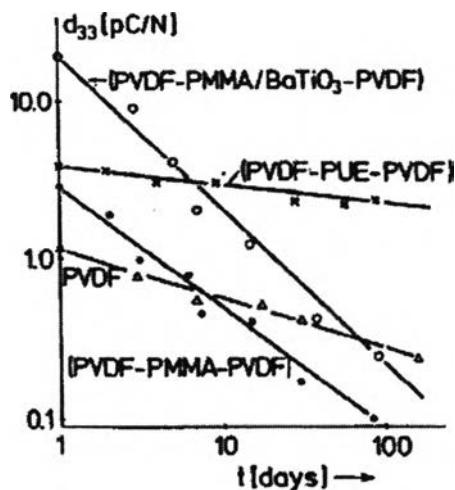


Figure 2.5 Time dependence of piezoelectric strain constant $d_{33}(t)$ of polarized films.

Figure 2.5 shows time dependencies of these constants are presented in. The initial values of d_{33} are 1, 3, 4 and 20 pC/N for PVDF, PVDF-PUE-PVDF, PVDF-PMMA-PVDF and PVDF-PMMA/BaTiO₃-PVDF, respectively. It can be concluded that the initial piezoelectric constant d_{33} is highest for PVDF-PMMA/BaTiO₃-PVDF system however, the better piezoelectric stability can be obtained in polarized PVDF-PUE-PVDF laminate (Mazur, 1992).

Laminated film having one or more ferro- or piezoelectric properties superior to those of individual polymeric films which are component of the laminated film. It is desired that the improvement in one or more of ferro- or piezoelectric properties be at least 20, 30 or 40 percent over the corresponding property of the individual component film layer. The piezoelectric strain constant d_{31} , piezoelectric stress constant e_{31} and remanent polarization, P_r of Nylon 11-PVDF bilaminated film were investigated compare to those of individual Nylon 11 and PVDF film [Scheinbiem, *et al.*, 1994].

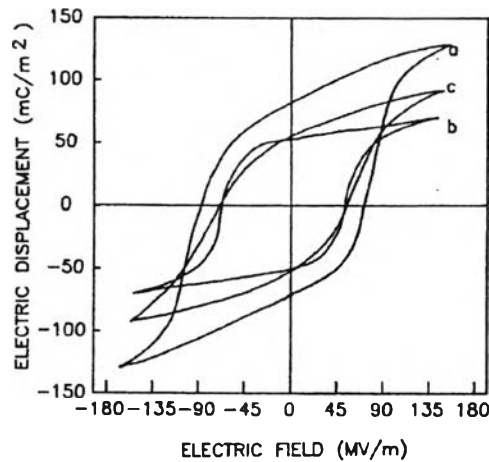


Figure 2.6 *D-E* hysteresis loop of Nylon 11-PVDF bilaminated film (a), Nylon 11 film (b) and PVDF film (c).

The result shows that the provided Nylon 11-PVDF bilaminated film are ferroelectric with clear *D-E* hysteresis loop. The Nylon 11-PVDF bilaminated film show significantly higher remanent polarization, P_r , which is 44% higher than that of either Nylon 11 or PVDF film, which were produced in an identical procedure. The piezoelectric strain constant, d_{31} , and piezoelectric stress constant, e_{31} of Nylon 11-PVDF bilaminated film show significant improvement at both room and evaluated temperatures when compare with Nylon 11 or PVDF film.

2.4 Laminated Poly(vinylidene fluoride) Film Applications

Multilayer ultrasound transducers in PVDF were first proposed by Swartz *et al.*, (1980) to be able to increase the acoustic output compared with conventional single-layer transducers. While PVDF has lower k_T and dielectric constants than ceramic piezoelectric materials, consequences of these weaknesses can be minimized by use of multilayer structures which can improve the power output from a voltage source-driven PVDF transducers. To build a PVDF transducer that delivers maximum output acoustic power from a voltage-source drive, the minimum layer thickness available should be selected and then these layers stacked until the composite is quarter-wave resonant at the desired operating frequency.

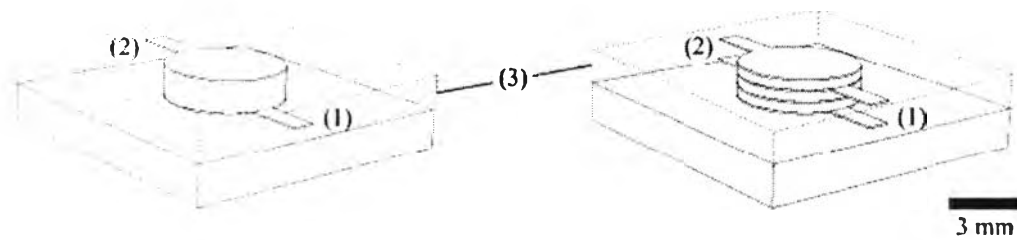


Figure 2.7 Sketch of single- and multilayer transducers showing signal (1) and ground (2) electrodes, with a circular diameter of 6.2 mm, embedded in the copolymer layer (3). The thickness of the polymer layer is exaggerated for clarity.

Following, Lilliehorn *et. al.*, (2005) made multilayer transducers of piezoelectric poly(vinylidene fluoridetrifluorethylene) (P(VDF-TrFE)) polymer without need of adhesive lamination by using spin coating technique as shown in figure 2.7. A comparison between single- and multilayer transducers of the same dimensions, fabricated using similar processing schemes, showed that the round trip insertion losses were 12 dB lower for the multilayer transducers than for corresponding single-layer transducers. Moreover, the multilayer PVDF transducer gave improvement of bandwidth properties as a figure 2.8 shown below. Multilayer PVDF transducer, 11-layer switchable PVDF copolymer Barker coded transducer, is better than the conventional PZT transducer in terms of insertion loss [Sitting, 1971], bandwidth and sensitivity. In particular, the Barker coded transducer provides a round trip insertion loss comparable with that of the PZT transducer but in a significantly wider bandwidth. This bandwidth is two times wider than that of the PZT transducer Zhang [*et. al.*, 1993].

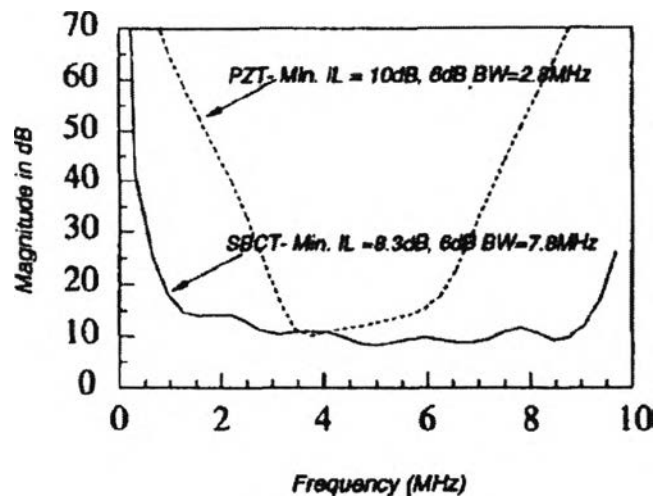


Figure 2.8 A comprehensive two-way insertion loss comparison between a switchable pulse-echo Barker coded transducer (SBCT) and an optimized 5 MHz PZT transducer.

The lamination of PVDF films allowed two objectives to be achieved. Firstly, the sensitivity of the element was increased. In principle, a laminate of three layers of 25- μm PVDF would have three times the sensitivity of a single layer of 25- μm PVDF (neglecting any second-order effects from the laminating process itself). Secondly, it was possible to create a screened structure by means of a “dual stack” approach: taking two pieces of polarized PVDF with gold live and earth electrodes formed on them and laminating them together with the live electrode surfaces in contact. The effect here was to create an electrically screened structure with earth electrodes on the external surfaces and the live electrode in the middle of the laminate. Another application which used laminated PVDF structures is hydrophone. Lamination of PVDF has provided the opportunity of designing and producing hydrophones with enhanced performance properties. Robinson *et al.*, (2000) developed hydrophone by using laminated PVDF, mechanically drawn to provide a microstructure suitable for strong piezoelectricity, was available only in a limited range of thicknesses. The approach adopted was to create thick PVDF films by lamination from thinner base film (usually 25- μm PVDF, which was readily available

as a good quality film). This structure can improve inherent sensitivity and acoustic impedance match to water.

Materials with high breakdown field strength (E_b) are useful in HV energy storage devices, power transmission cables and other devices. Several approaches have been tried in the past to increase the E_b : (1) increase the physical strength since in thin films it is well established that mechanical failure is related to electrical strength, (2) decrease the defect density, and (3) optimize the morphology of the dielectric. Zheng *et al.*, (1996) The enhancement of dc E_b obtained on some polymer film after being coated with PVDF thin films was found to be insensitive to the thickness of the polymer films and the thickness of PVDF coatings. For PEN, PEI and PET laminates, the E_b increased by as much as 8, 16 and 18%, respectively. And also the dielectric properties for various polymer coated with PVDF thin films increased significantly. Moreover, The interface between the metal electrode and PVDF is very important to the dc breakdown of PVDF [Zheng *et al.*, 2000].

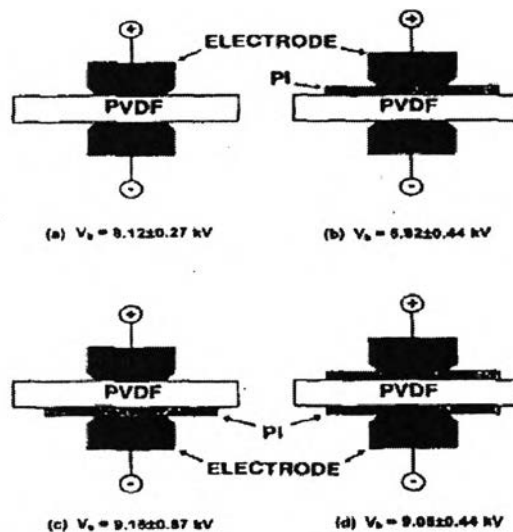


Figure 2.9 Four PVDF films with different interfaces to the metal electrodes. The thicknesses of PVDF and PI films are 11 μm and 2 μm , respectively.

When the positive charge of the metal electrode was blocked by an inserting polymer film between the PVDF and the electrode, the breakdown voltage was reduced. This dependence of dielectric breakdown on metal-PVDF interface is

believed to relate directly to the different surface charge densities at surfaces of PVDF films.