CHAPTER I
INTRODUCTION

1.1 Statement of Thesis Purpose

Polymer–ceramic composites combine superior properties of both polymers and ceramics which results in far better performance than those of the constituent materials [Adikarya, S.U.,*et al.* 2002]. They have received much attention as new piezoelectric materials for applications in electromechanical transducer, above all microphones and hydrophones, medical ultrasound as well as pyroelectric detector,etc. Polymers are flexible, easy to fabricate and superior in dielectric break down strength. Otherwise, ferroelectric ceramics possess high dielectric permittivity but with poor mechanical properties and lower dielectric breakdown strength. By integrating high dielectric permittivity ceramic powder with superior dielectric strength of the polymer, one can develop a composite with high dielectric permittivity and high breakdown strength. Piezoelectric activity of polymer/ceramic composites depends on the content of ceramic component and on polarizing conditions [Olszowy, M. 1997]. This type of composites has high capability of energy storage and can be used in capacitors and energy storage devices. The easiness of composite fabrication allows producing thin film capacitors which is difficult to achieve in ceramics due to complicated fabrication routes.

In this study, PVDF film (poly vinylidene fluoride) was used as a piezoelectric polymer. The dielectric constant of PVDF is higher than most polymers, and makes PVDF attractive for integration into devices as the signal to noise ratio is less for higher dielectric materials. The most stable, non-polar phase results upon casting PVDF from the melt and can be transformed into the polar phase by mechanically stretching. Kawai showed that thin films that had been poled exhibited a very large piezoelectric coefficient, 6-7 pCN^{-1}, a value which is about ten times larger than had been observed in any other polymer [Harrison, J.S., *et al.* 2001]. The weak points of PVDF are possessed low the dielectric constant compare to those of ceramic and exhibit relaxation behavior. From these concerns, the composite of PVDF and ceramic with high dielectric constant would be expected to have higher dielectric constant and less relaxation behavior.

BST (barium strontium titanate) was used as ferroelectric ceramic because of capability in wide applications in many electronic applications (Lu, Q., *et al.* 2003) BST is of high interest since it provides a unique combination of high dielectric constant, low dc leakage, low loss tangent up to high frequencies, and stable operation at high temperatures. $Ba_{(1-x)}Sr_xTiO_3$ (BST) is the solid solution of $BaTiO_3$ and $SrTiO_3$, which belong to the general class of ferroelectric materials based on the perovskite structure [Wua, D., *et al.* 2000]. Barium titanate ($BaTiO_3$) and its related compounds have been extensively used in the preparation of high dielectric capacitors, positive temperature coefficient (PTC) resistors, transducers and ferroelectric memories. The substitution of strontium for barium and desirable properties can be obtained such as high dielectric permitivity and low loss factor at room temperature. BST have been prepared by variety of methods. Among these methods, sol–gel processing offers some advantages over other methods in terms of low-temperature preparation, compositional homogeneity, purity (because of the liquid form of precursors which can be easily purified by distillation), cost effective and simple[Nayak, M., *et al.* 2000]. The weak points of BST are hard fabrication and low dielectric break down. By mixing BST in a polymer matrix, the dielectric breakdown and the difficulty in fabrication would be improved

PVDF-BST composites combine superior properties of both PVDF and BST which results in far better performance than those of the constituent materials. The composites will be expected to have high dielectric constant, high dielectric breakdown, and less relaxation. Another importance is easier composite fabrication allowing producing thick film sensors which are difficult to achieve in ceramics due to complicated fabrication routes.

In the present study, we investigate the electric and dielectric properties of PVDF/ $Ba_{0.7}Sr_{0.3}TiO_3$ film which is 0-3 connectivity. Not much work has been done on composite between PVDF/$Ba_{0.7}Sr_{0.3}TiO_3$ and there is a minimal report on their electrical and dielectric properties.

1.2 Theoretical Background

Upon reviewing the abundance of literature on the subject, it is clear that there is no standard definition for smart materials, and that terms such as intelligent materials, smart materials, adaptive materials, active devices, and smart systems, are often used interchangeably. The term smart material generally designates a material that changes one or more of its properties in response to an external stimulus. The most popular smart material systems are piezoelectric materials, magnetostrictive materials, shape memory alloys, electrorheological fluids, electrostrictive materials and optical fibers. Magnetostrictives, electrostrictives, shape memory alloys and electrorheological fluids are used as actuators while optical fibers are used primarily as sensors. Among these active materials, piezoelectric materials are most widely used because of their wide bandwidth, fast electromechanical response, relatively low power requirements and high generative forces. A classical definition of piezoelectricity, a Greek term for pressure electricity, is the generation of electrical polarization in a material in response to a mechanical stress. This phenomenon is known as the direct effect which is used in sensing applications, such as in force or displacement sensors. Piezoelectric materials also display the converse effect; mechanical deformation upon application of electrical charge or signal The inverse piezoelectric effect is used in actuation applications, such as in motors and devices that precisely control positioning, and in generating sonic and ultrasonic signals. The direct and converse piezoelectric effects can be expressed in tensor notation.

$$P_i = d_{ijk}\, s_{jk} \text{ (Direct Effect)} \qquad (1)$$

$$e_{ij}=d_{kij}\, E_k \text{ (Converse Effect)} \qquad (2)$$

where P_i is the polarization generated along the i- axis in response to the applied stress s_{jk}, and d_{kij} is the piezoelectric coefficient. For the converse effect, e_{ij} is the strain generated in a particular orientation of the crystal on the application of electric field E_i along the i-axis. Piezoelectricity is a property of many non-centrosymmetric ceramics, polymers and other biological systems. A subset of piezoelectricity is pyroelectricity, whereby the polarization functions of temperature. Some pyroelectric materials are ferroelectric, although not all ferroelectrics are pyroelectric. Ferroelectricity is a property of certain dielectrics, which exhibit a spontaneous electric polarization (separation of the center of positive and negative electric charge, making one side of the crystal positive and the opposite side negative) that can be reversed in direction by the application of an appropriate electric field. Ferroelectricity is named by analogy with ferromagnetism, which occurs in materials such as iron. Traditionally, ferroelectricity is defined for crystalline materials, or at least in the crystalline region of semicrystalline materials. [Harrison, J.S. (2001)](Figure 1.1)

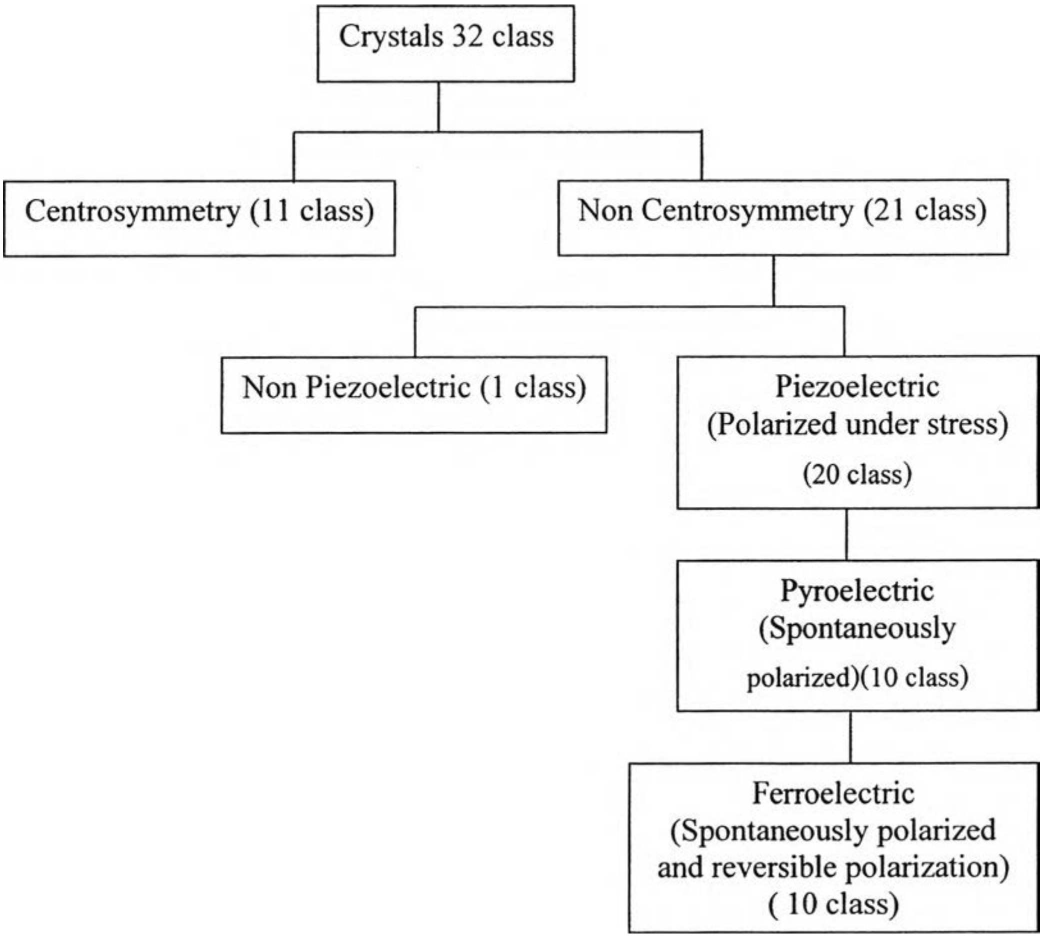


Figure 1.1 System of crystals in 32 class.

1.2.1 Piezoelectric Ceramic

In the 20th century metal oxide-based piezoelectric ceramics and other man-made materials enabled designers to employ the piezoelectric effect and the inverse piezoelectric effect in many new applications. These materials generally are physically strong and chemically inert, and they are relatively inexpensive to manufacture. The composition, shape, and dimensions of a piezoelectric ceramic element can be tailored to meet the requirements of a specific purpose.

A traditional piezoelectric ceramic is a mass of perovskite crystals, each consisting of a small, tetravalent metal ion, usually titanium or zirconium, in a lattice of larger, divalent metal ions, usually lead or barium, and O_2 ions.Under conditions that confer tetragonal or rhombohedral symmetry on the crystals, each crystal has a dipole moment.Above a critical temperature, the Curie point, each perovskite crystal in the fired ceramic element exhibits a simple cubic symmetry with no dipole moment (Figure 1.2a). At temperatures below the Curie point, however, each crystal has tetragonal or rhombohedral symmetry and a dipole moment (Figure 1.2b). Adjoining dipoles form regions of local alignment called domains. The alignment gives a net dipole moment to the domain, and thus a net polarization. The direction of polarization among neighboring domains is random, however, so the ceramic element has no overall polarization (Figure 1.3a).

The domains in a ceramic element are aligned by exposing the element to a strong, direct current electric field, usually at a temperature slightly below the Curie point (Figure 1.3b). Through this polarizing (poling) treatment, domains most nearly aligned with the electric field expand .When the electric field is removed most of the dipoles are locked into a configuration of near alignment (Figure 1.3c). The element now has a permanent polarization, the remanent polarization, and is permanently elongated. electricfield to a piezoelectric ceramic element until maximum polarization, Ps , is attained, reducing the field to zero to determine the remanent polarization, Pr , reversing the field to attain a analogous to corresponding characteristics of ferromagnetic materials, a poled ferroelectric material exhibits hysteresis. Figure 1.4 shows a typical hysteresis curve created by applying an negative maximum polarization.

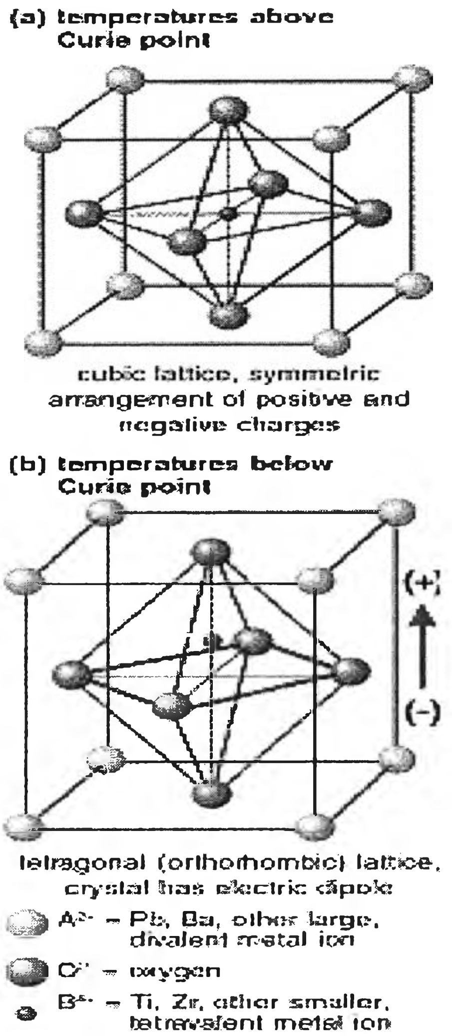


Figure 1.2 Crystal structure of tradition piezoelectric.

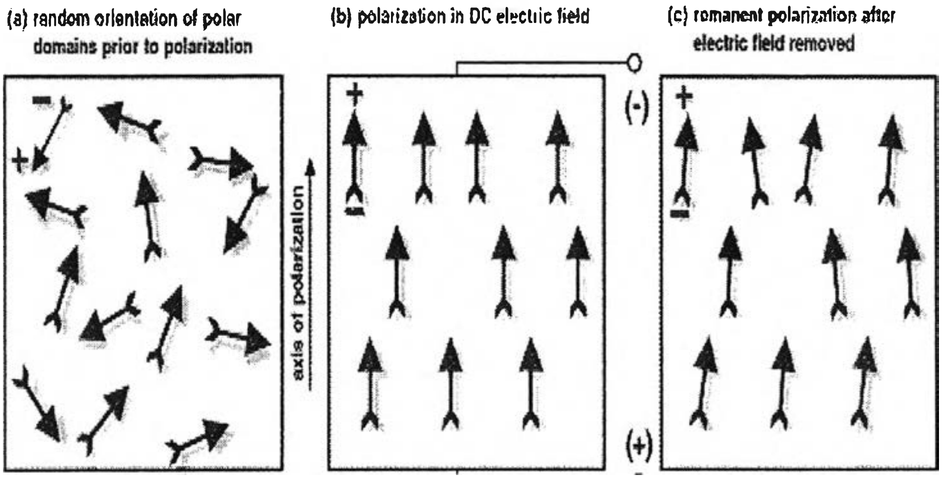


Figure 1.3 Polarizing (poling) a piezoelectric ceramic.

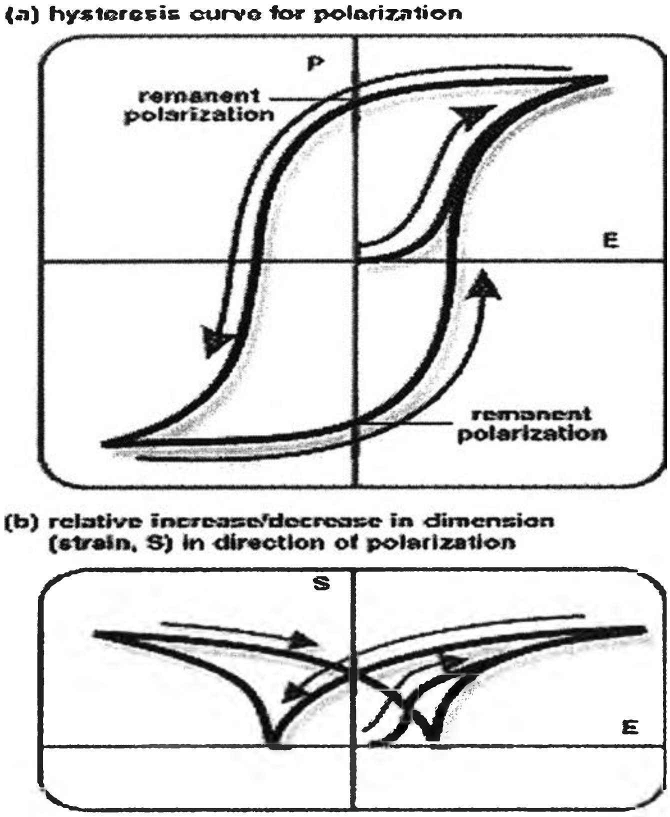
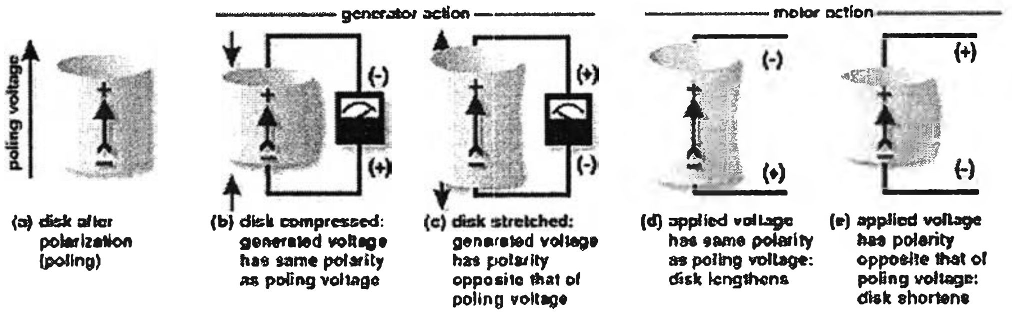


Figure 1.4 Effects of Electric Field (E) on Polarization (P) and Corresponding Elongation / Contraction of a Ceramic Element.

remanent polarization, and re-reversing the field to restore the positive remanent polarization. The tracing below the hysteresis curve plots the relative change in the dimension of the ceramic element along the direction of polarization, corresponding to the change in the electric field. The relative increase/decrease in the dimension parallel to the direction of the electric field is accompanied by a corresponding, but approximately 50% smaller, relative decrease/increase in the dimension perpendicular to the electric field.

Mechanical compression or tension on a poled piezoelectric ceramic element changes the dipole moment, creating a voltage. Compression along the direction of polarization, or tension perpendicular to the direction of polarization, generates voltage of the same polarity as the poling voltage (Figure 1.5b). Tension along the direction of polarization, or compression perpendicular to the direction of polarization, generates a voltage with polarity opposite that of the poling voltage (Figure 1.5c). These actions are generator actions the ceramic element converts the mechanical energy of compression or tension into electrical energy. This behavior is used in fuel-igniting devices, solid state batteries, force-sensing devices, and other products. Values for compressive stress and the voltage (or field strength) generated by applying stress to a piezoelectric ceramic element are linearly proportional up to a material-specific stress. The same is true for applied voltage and generated strain.

If a voltage of the same polarity as the poling voltage is applied to a ceramic element, in the direction of the poling voltage, the element will lengthen and its diameter will become smaller (Figure 1.5d). If a voltage of polarity opposite that of the poling voltage is applied, the element will become shorter and broader (Figure 1.5e). If an alternating voltage is applied, the element will lengthen and shorten cyclically, at the frequency of the applied voltage. This is motor action electrical energy is converted into mechanical energy. The principle is adapted to piezoelectric motors, sound or ultrasound generating devices, and many other products.



(a) disk after polarization (poling)

(b) disk compressed: generated voltage has same polarity as poling voltage

(c) disk stretched: generated voltage has polarity opposite that of poling voltage

(d) applied voltage has same polarity as poling voltage: disk lengthens

(e) applied voltage has polarity opposite that of poling voltage: disk shortens

Figure 1.5 Generator and motor actions of a piezoelectric element generator action is used in fuel-igniting devices, solid state batteries, and other products; motor action is adapted to piezoelectric motors, sound or ultrasound generating devices, and many other products.

1.2.1.1 Perovskites

Perovskite is a family name of a group of materials and the mineral name of calcium titanate ($CaTiO_3$) having a structure of the type ABO_3. Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate ($KNbO_3$), Potassium Sodium Niobate ($K_xNa_{1-x}NbO_3$), and Potassium Tantalate Niobate ($K(Ta_xNb_{1-x})O_3$) have a perovskite type structure.

Barium Titatate ($BaTiO_3$, BT)

Barium titanate ($BaTiO_3$) has a paraelectric cubic phase above its Curie point of about 130 °C In the temperature range of 130°C to 0 °C the ferroelectric tetragonal phase with a c/a ratio of ~1.01 is stable. The spontaneous polarization is along one of the [001] directions in the original cubic structure. Between 0 °C and -90 °C , the ferroelectric orthorhombic phase is stable with the polarization along one of the [110] directions in the original cubic structure(see Fig1.6). On decreasing the temperature below -90 °C the phase transition from the orthorhombic to ferroelectric rhombohedral phase leads to polarization along one of the [111] cubic directions.The spontaneous polarization on cooling $BaTiO_3$ below the Curie point T_c is due to changes in the crystal structure. As shown in Fig. 1.7 the paraelectric cubic phase is stable above 130 °C with the center of positive charges

(Ba^{2+} and Ti^{4+} ions) coinciding with the center of negative charge (O^{2-}). On cooling below the Curie point T_C, a tetragonal structure develops where the center of Ba^{2+} and Ti^{4+} ions are displaced relative to the O^{2-} ions, leading to the formation of electric . Various A and B site substitutions in different concentrations have been tried to see their effect on the dielectric and ferroelectric properties of $BaTiO_3$. Sr^{2+} substitutions to the A site have been found to reduce the Curie point linearly towards room temperature. The simultaneous substitution into both A and B sites with different ions can be used to tailor the properties of $BaTiO_3$.

The effect of various isovalent substitutions on the transition temperatures of $BaTiO_3$ ceramic are shown in Fig. 1.8

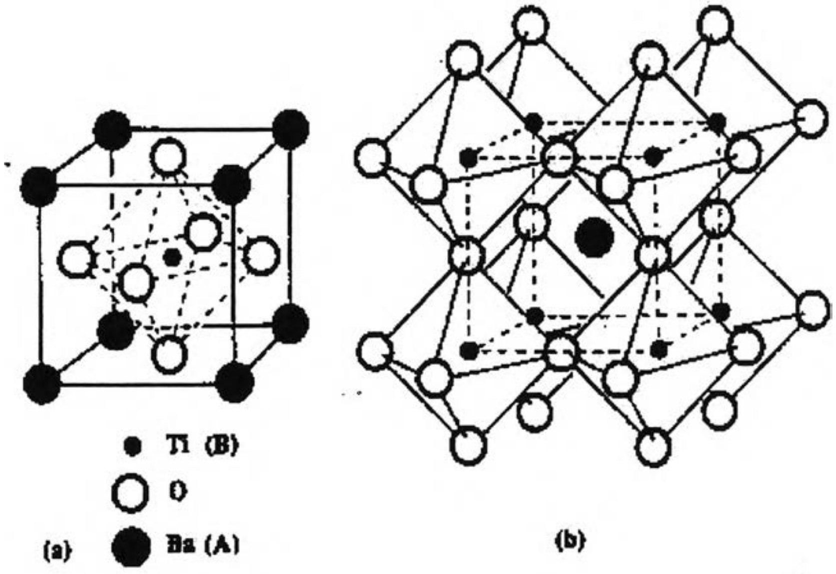


Figure 1.6 (a) A cubic ABO_3 ($BaTiO_3$) perovskite-type unit cell and (b) three dimensional network of corner sharing octahedra of O^{2-} ions [12].

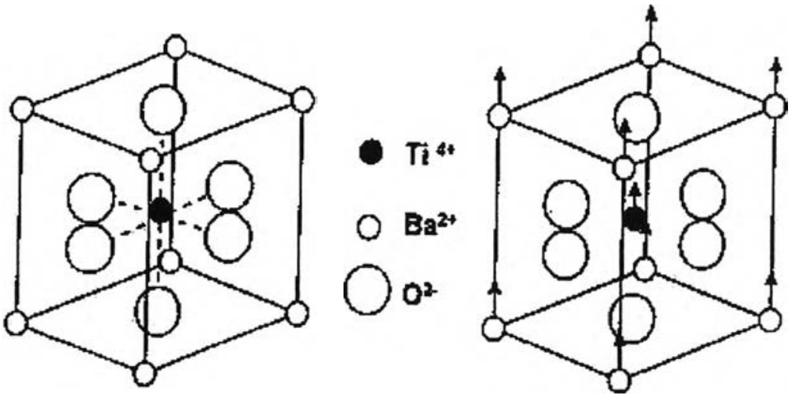


Figure 1.7 The crystal structure of $BaTiO_3$ (a) above the Curie point the cell is cubic; (b) below the Curie point the structure is tetragonal with Ba^{2+} and Ti^{4+} ions displaced relative to O^{2-} ions.

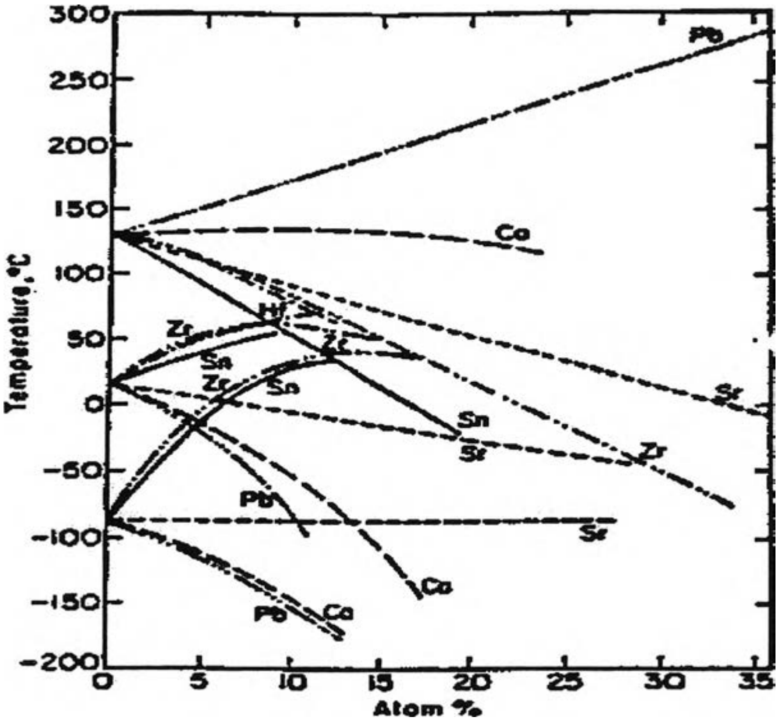


Figure 1.8 The effect of isovalent substitutions on the transition temperatures of BT ceramic.

From Figure 1.8, please be noted that the curie point of barium titanate is decrease linearly by the substitution of strontium for barium and desirable properties can be obtained such as a high dielectric permittivity and low loss factor at room temperature. The properties of barium strontium titanate (BST) can therefore be tailored for specific applications.

1.2.2 Piezoelectric Polymer

The existence of piezoelectric polymers was already known since 1924. However, the early known piezoelectric polymers did not receive much attention until the work by Fukada in the fifties and sixties .Fukada and his co-workers discovered that rolled films of polypeptides and numerous other polymers induce surface charges when stressed. A major milestone in this field was recorded with the Kawai's discovery of the strong piezoelectric effect in polyvinylidene fluoride (PVDF or PVF2) in 1969 [Kawai, 1969]. Later, other PVDF co-polymers were also reported, including P(VDF-TrFE) and P(VDF-TeFE) and others. [Bar-Cohen, Y., (1996)].

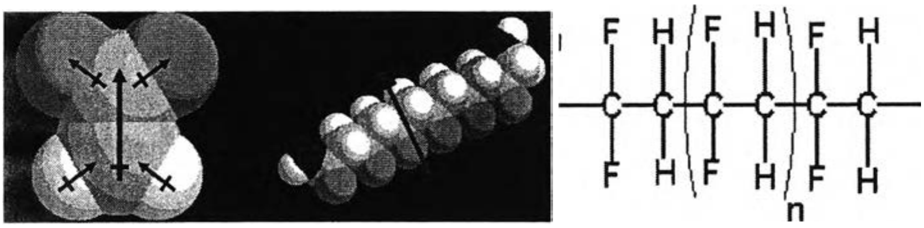


Figure 1.9 Structure of PVDF

1.2.2.1 Characteristics of Piezoelectric Polymers

The properties of polymers are so different in comparison to inorganics (Table 1.1) that they are uniquely qualified to fill niche areas where single crystals and ceramics are incapable of performing as effectively. As noted in Table 1.1, the piezoelectric strain constant(d_{31}) for the polymer is lower than that of the ceramic. However, piezoelectric polymers have much higher piezoelectric stress constants (g_{31}) indicating that they are much better sensors than ceramics. Piezoelectric polymeric sensors and actuators offer the advantage of processing flexibility because they are lightweight, tough, readily manufactured into large areas, and can be cut and formed into complex shapes. Polymers also exhibit high strength and high impact resistance. Other notable features of polymers are low dielectric constant, 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). 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. Polymers offer the ability to pattern electrodes on the film surface, and pole only selected regions. Based on these features, piezoelectric polymers possess their own established area for technical applications and useful device configurations, d_{31} [Harrison, J.S. (2001)]

Table 1.1 Property comparison for standard piezoelectric polymer and ceramic materials

	d_{31} (pm/V)	g_{31} (mV-m/N)	k_{31}	
Polyvinylidenefluoride PVDF	28	240	0.12	flexible, lightweight, low acoustic and mechanical impedance
Lead Zirconium Titanate PZT	175	11	0.34	brittle, heavy, toxic

1.2.2.2 Structural Requirements for Piezoelectric Polymers.

The following sections explain piezoelectric mechanisms for both semicrystalline and amorphous polymers. Although there are distinct differences, particularly with respect to polarization stability, in the simplest terms, four critical elements exist for all piezoelectric polymers, regardless of morphology. As summarized by Broadhurst and Davis these essential elements are: (a) the presence of permanent molecular dipoles; (b) the ability to orient or align the molecular dipoles; (c) the ability to sustain this dipole alignment once it is achieved; and (d) the ability of the material to undergo large strains when mechanically stressed.

Mechanism of piezoelectricity in semicrystalline polymers

In order to render piezoelectric, semicrystalline polymers must have a polar crystalline phase. The morphology of such polymers consists of crystallites dispersed within amorphous regions as shown in Figure 1.10.The amorphous region has a glass transition temperature that dictates the mechanical properties of the polymer while the crystallites have a melting temperature that dictates the upper limit of the use temperature.

The degree of crystallinity present in such polymers depends on their method of preparation and thermal history. Most semicrystalline polymers have several polymorphic phases, some of which may be polar. Mechanical orientation, thermal annealing and high voltage treatment have all been shown to be effective in inducing crystalline phase transformations. Stretching the polymer essentially aligns the amorphous strands in the film plane as shown in Figure 1.10 b and facilitates uniform rotation of the crystallites by an electric field. Depending on whether stretching is uniaxial or biaxial, the electrical an mechanical properties and therefore the transduction response), are either highly anisotropic or isotropic in the plane of the polymer sheet. Electrical poling is accomplished by applying an electric field across the thickness of the polymer as depicted in Figure 1.10 c. An electric field on the order of 50 MV/m is typically sufficient to effect crystalline orientation. For semicrystalline polymers the amorphous phase supports the crystal orientation and the polarization is stable up to the Curie temperature.

This polarization can remain constant for many years if it is not influenced by the spurious effects of moisture uptake or elevated temperature

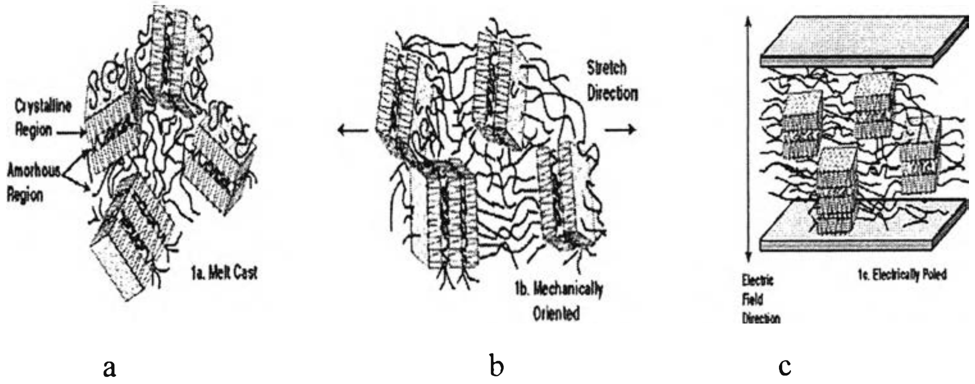


Figure 1.10 Random stacks of amorphous and crystal lamellae in PVDF polymer. (a) represents the morphology after the film is melt cast; (b) is after orientation of the film by mechanically stretching to several times its original length; (c) is after depositing metal electrodes and poling through the film thickness.

Ferroelectricity in semicrystalline polymers

At high electric fields, the polarization that occurs in semicrystalline polymers such as PVDF is nonlinear with the applied electric field. This nonlinearity in polarization is defined as hysteresis. The existence of a spontaneous polarization together with polarization reversal (as illustrated by a hysteresis loop) is generally accepted as proof of ferroelectricity. Figure 1.11 is an example of the typical hysteresis behavior of PVDF. Two other key properties typically reported for ferroelectric materials are the coercive field and the remanent polarization. The coercive field, *Ec,* which marks the point where the hysteresis intersects with the horizontal axis, is typically about 50 MV/m at room temperature for many ferroelectric polymers. The remanent polarization, *Pr,* corresponds to the point where the loop intersects with the vertical axis. The values of *Ec* and *Pr* are dependent on the temperature and frequency of measurement. The Curie temperature *Tc,* is generally lower than but close to the melting temperature of the polymer. Below *Tc,* the polymer is ferroelectric and above *Tc,* the polymer loses its non-centrosymmetric nature.

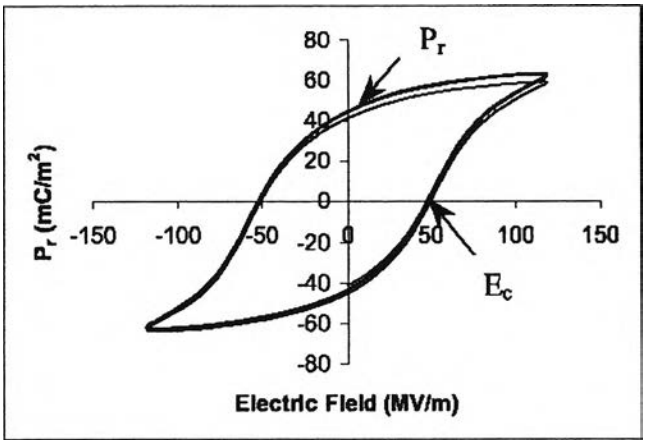


Figure 1.11 Typical ferroelectric hysteresis loop for PVDF.

The origin of piezoelectricity in PVDF is not well understood and the "dipole model" is the most widely accepted explanation of its origin. This material is a semi-crystalline high-molecular weight polymer with repeat unit (CH_2 - CF_2) whose structure is essentially head-to-tail, i.e., CH_2 - CF_2 - (CH_2-CF_2) n - CH_2 - CF_2. PVDF is approximately half crystalline and half amorphous. The crystalline form consist of a non-polar *alpha* phase and a highly polar β phase (See Figure 1.12). Where the α phase is a non-polar phase, whereas the *beta* phase has the hydrogen and fluorine atoms arranged to give maximum dipole moment per unit cell. These dipole moments are randomly oriented until the polymer is electrically polarized. Under the application of an electric field, the polymer chains inside the crystallites align themselves along the field by rotating the dipoles around the chain axis. The piezoelectric response of PVDF polymers is the result of a net polarization.

PVDF demonstrates hysteresis loops similar to those known from crystalline ferroelectric materials [Wang, Herbert and Glass, 1988]. As can be seen from Table 1.2, this polymer demonstrates piezoelectric constant, d_{33},of more than -30 pC/N which is very high. The constant d_{33} is negative, in other words, applying an electric

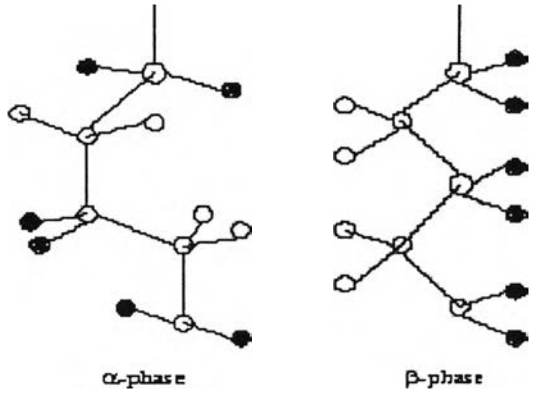


Figure 1.12 Two of the PVDF phases. The *alpha*-phase consists of a series of non-polar anti-parallel chains, whereas *beta*-phase phase consists of a series of polar parallel chain.

field in the direction of polarization (film thickness) causes the film thickness to decrease. PVDF has an anisotropic piezoelectric characteristics, where in the film plane the strongest effect is in the drawing direction as opposed to the normal direction, i.e., $d_{31} > d_{32} > 0$. The ratio of these two d-constants can vary between 5 to 10 times. In Table 1.2, comparison is given between the properties of PVDF and some of the commonly used piezoelectric materials. While PVDF has a relatively low dielectric ratio, compared to piezoelectric ceramics and crystalline materials, this ratio is relatively higher compared to other polymers (Figure 1.13).

Table 1.2 Comparison between commonly used crystalline piezoelectric materials and PVDF

Material	Relative Dielectric constant $\varepsilon/\varepsilon o$	Piezoelectric constant d_{33}	Piezo strain/volt const. g_{33}
BT	1700	191	12.6
Quartz	4.5	2.3(d11)	50.0(g31)
PVDF	13	-33	-339
PZT-4	1300	289	25.1

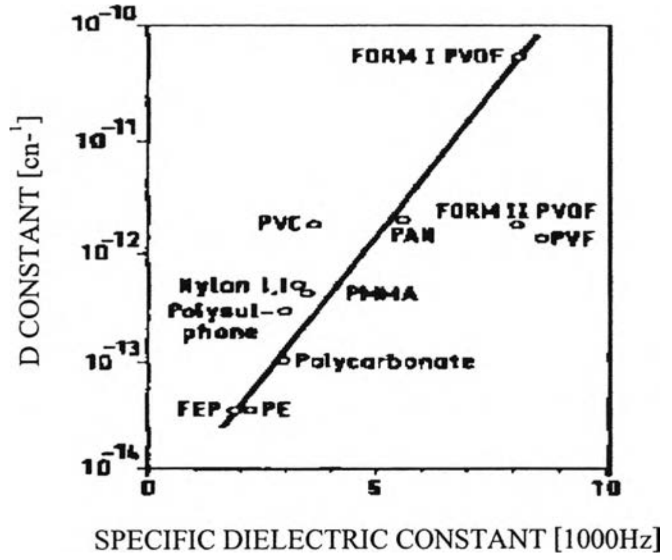


Figure 1.13 Piezoelectric *d* constant as function of dielectric permittivity. Abbreviations: PVC (polyvinylehloride), PAN (poiyacryionitrite), PVF (polyvinylfluouride), PMMA (polymethylmethacrylate), FEP (fluorinated ethylenepropylene),and PE (polyethylene).

1.2.3 Piezoelectric Composite

Composite materials (or composites for short) are engineered materials made from two or more constituent materials that remain separate and distinct on a macroscopic level while forming a single component.There are two categories of constituent materials: matrix and reinforcement. At least one portion (fraction) of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart special physical (mechanical and electrical) properties to enhance the matrix properties. Due to the wide variety of matrix and reinforcement materials available, the design potential is incredible The drive for piezoelectric composites stems from the fact that desirable properties could not be obtained from single phase materials such as piezoceramics or piezopolymers. For example, in an electromechanical transducer, the desire is to maximize the piezoelectric sensitivity, minimize the density to obtain good acoustic matching with water, and make the transducer mechanically flexible to conform to a curved surface. Neither a ceramic nor a polymer satisfies these requirements. The requirement can be optimized by combining the most useful properties of the two phases which do not ordinarily appear together.

Piezoelectric composites are made up of an active ceramic phase embedded in a passive polymer. The properties of the composite depend on the connectivity of the phases, volume percent of ceramic, and the spatial distribution of the active phase in the composite. The concept of connectivity developed by Newnham *et al.*, describes the arrangement of the component phases within a composite. It is critical in determining the electromechanical properties of the composite. Figure 1.14 shows the 10 different types of connectivity possible in a diphasic composite. It is shown in the form A-B where 'A' refers to the number of directions in which the active phase is self connected or continuous. 'B' shows the continuity directions of the passive phase. The density, acoustic impedance, dielectric constant and the piezoelectric properties like the electromechanical coupling coefficient k_t change with the volume fraction of the ceramic. Many excellent reviews on the processing and properties of piezoelectric / polymer composites have been written in the last few years.

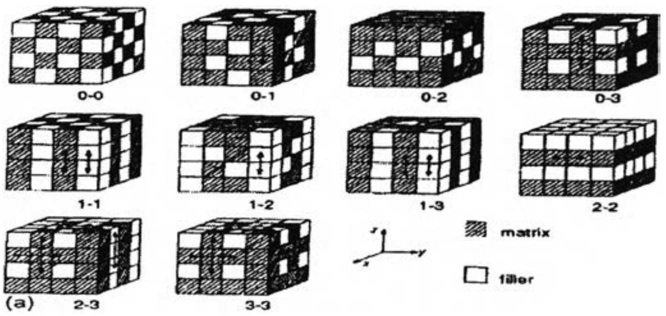


Figure 1.14 Connectivity patterns for a diphasic solid A-B. The shaded parts represent the A phase while the white parts show the B phase.

0-3 Connectivity Composite patterns

Basically, a composite with 0-3 connectivity consists of particles connected in zero dimensions and a three dimensionally interconnected polymer matrix as shown in Figure 1.15

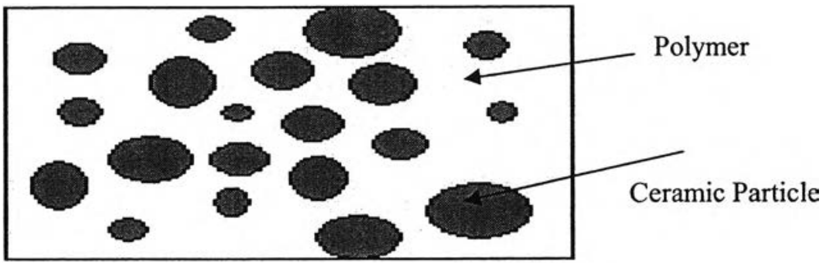


Figure 1.15 0-3 composite: the separated ceramic particles randomly dispersed in a host polymer matrix.

By the use of the right proportion of the constituent materials, the composite with 0-3 configuration can be fabricated with ease. The following equations are used to prepare quantities required for mixing of ceramic and polymer [Lang, S.B. 2000].

$$M^{P} = M^{C}\frac{\rho^{P}}{\rho^{C}}\left(\frac{1-\phi}{\phi}\right) \qquad (1)$$

Where M, ρ and ϕ are the mass, density and volume fractions respectively, and the superscripts p and C refer to polymer and ceramic respectively. The density ρ of the composite is determined thus,

$$\rho = \phi\rho^{C} + (1-\phi)\rho^{P} \qquad (2)$$

and the total composite volume V is given by

$$V = \frac{M^{C}}{\phi\rho^{C}} \qquad (3)$$

In describing composite properties with low volume fraction of the ceramic powder dispersed in the host polymer, the Pauer cube model (Figure 1.16) is applicable .In this model, a unit cube represents the volume of the composite. Within this cube there is a smaller cube of dimension *m*, which represents the volume fraction of the ceramic. Using this model, the ceramic grain size should not be comparable to the film thickness and then the ceramic volume fraction ϕ^C, is given by [Das-Gupta, D.K. 1994].

$$\phi^C = m^3 \tag{4}$$

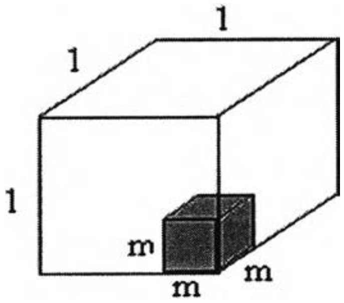


Figure 1.16 Pauer cube model for 0-3 composites.