Chapter 2

Literature Survey

2.1 Piezoelectricity

Piezoelectric materials have the property that dielectric polarization, and associated charge, are developed when a stress is applied. These materials also exhibit a converse effect which involves a charge in dimensions when an electric field is applied. Fundamental research has shown that piezoelectricity is based on a property of the elementary unit cell of the crystalline structure of the material, the essential condition being that the crystal unit cell should have no center of symmetry[1].

Of 32 crystal classes, 11 are centrosymmetric and consequently cannot exhibit polar properties[2]. One of the remaining 21 noncentrosymmetric classes (cubic 432) has symmetry elements which prevent polar characteristics. The other 20 classes have one or more polar axes and thus can exhibit piezoelectricity.

Of the 20 piezoelectric classes of crystals, 10 have unique polar axes. These classes are called polar crystals because they are spontaneously polarized and exhibit pyroelectricity. However, ferroelectric crystals are only those crystals for which the spontaneous polarization can be reversed by applying an electric field. In order to produce the piezoelectric effect, the application of an electric field is required so that the dipoles are aligned and a net polarization can be obtained. Two effects are manifest in piezoelectricity: the direct effect and converse effect. The direct effect refers to the phenomenon that occurs when the surface electrical charge (polarization) is generated from a mechanical stress, whereas the converse effect is associated with a dimensional charge initiated by the application of an electrical field.

The direct piezoelectric effect is described using the matrix notation,

$$P_i = d_{ij}\sigma_j \qquad (2.1)$$

$$i = 1,2,3$$

$$j = 1,2,3,4,5,6$$

where, P_i are the electrical polarizations, σ_j are the applied mechanical stresses, and d_{ij} are the piezoelectric charge coefficients. The unit of d_{ij} is Coulomb/Newton.

In the set of piezoelectric constants, d_{ij}, the first subscript, i, designates the electrical direction (electric polarization or electric field), and the second subscript, j, identifies the mechanical direction (mechanical stress or strain). These subscripts are numbered, base on orthogonal axes with the x, y and z directions represented as 1, 2, and 3, respectively. The number 4, 5, and 6 refer to shear around the x, y, and z axes, respectively.

The converse piezoelectric effect is defined by the following relationship:

$$\varepsilon_{ij} = d_{ij}E_i \qquad (2.2)$$

$$i = 1,2,3$$

$$j = 1,2,3,4,5,6$$

where ε_{ij} are the induced mechanical strains and E_i are the electric field components.

An another set of constants used to characterize the piezoelectric effect are the piezoelectric voltage coefficients, g_{ij}, defined as:

$$E_i = g_{ij}\sigma_j \qquad (2.3)$$

$$i = 1,2,3$$

$$j = 1,2,3,4,5,6$$

where E_i are the electric fields that result from the applied stress σ_j. The g_{ij} coefficient has the unit of volt-meter/Newton.

The d_{ij} and g_{ij} are related to each other by the equation:

$$g_{ij} = d_{ij}/K_{ii}\varepsilon_0 \qquad (2.4)$$

$$i = 1,2,3$$

$$j = 1,2,3,4,5,6$$

where, K_{ii} are the dielectric constants and ε_0 is the permittivity of free space (8.854×10^{-12} Farad/meter).

The number of piezoelectric coefficients which describe all the possible piezoelectric effects in a given material depend upon the crystal class and space group to which it belongs[2]. For the triclinic asymmetric crystal class, all 18 coefficients are required. As the number of symmetry element increases, there is a corresponding decrease in the number of coefficients, because many are often equal to each other or zero.

The crystal symmetry of the poled piezoelectric ceramic material falls in the crystal class 6 mm. The only non-zero d_{ij} piezoelectric coefficients for this symmetry are d_{33}, $d_{31}(=d_{32})$, and d_{15}[2,3]. Also, when a charge is applied and crosses a piezoelectric material, it will elongate in the ploed direction but gets thinner in the other two directions. This implies that d_{33} is of opposite sign to d_{31} and d_{32} [Figure 2.1]

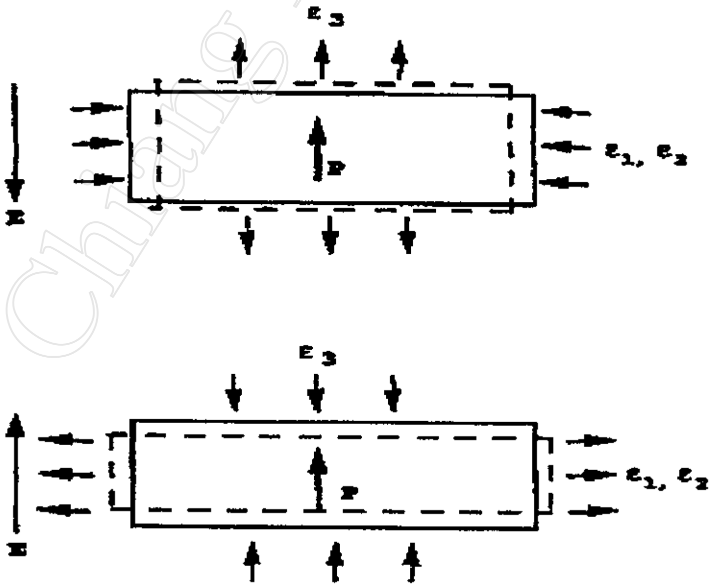

Figure 2.1 Schematic representation of piezoeletric response under the electric field E.

2.2 Piezoelectric Applications

The piezoelectric materials are used in a wide range of electromechanical transducers which convert energy into mechanical vibration and vice versa. The direct piezoelectric effect enables a transducer to function as a passive sound receiver by the conversion of acoustic energy into electrical signal. Applications include hydrophones, which are used to detect low frequency noises underwater, and microphones. The converse effect permits a transducer to act as an active sound transmitter or loud speaker. In particular, a piezotweeter is an audio speaker component used to generate high frequency sounds.

A transducer can also perform both active and passive functions simultaneously. When operated in a pulse-echo mode, a transducer element propagates an acoustic wave in a medium, then is capable of sensing echoes returning late. This technique was first utilized in 1916 as SONAR for submarine detection by Langevin[4]. Today, the operation of biomedical imaging and non-destructive testing devices is based on this principle, as a single transducer serves as both transmitter of a high frequency ultrasound beam and receiver of its echoes.

The optimum properties for a piezoelectric transducer are dependent on its specific application. The next two sections will examine the required properties of transducer materials used in different frequency ranges - (1) low frequency hydrophone and (2) high frequency biomedical imaging probes.

2.2.1 Hydrophone Applications

A hydrophone is an underwater microphone operated in a passive mode to detect underwater sound. The hydrophone is used in the low frequencies usually in a range below 40 kHz, where the dimensions of the piezoelectric samples are smaller than the acoustic wavelength[4]. Thus, the piezoelectric materials for this application respond to the hydrostatic pressure, where all surfaces are stressed with equal amplitude. This response can be expressed as[5] :

$$P_3 = (d_{33} + d_{31} + d_{32})(-p)$$

$$P_3 = (d_{33} + 2d_{31})(-p)$$

$$P_3 = d_h(-p) \qquad (2.5)$$

where P_3 is the electric polarization in the poled direction, d_h is the hydrostatic charge coefficient, and p is the hydrostatic pressure.

The following relationship also exists :

$$g_h = d_h/(\varepsilon_0 K), \qquad (2.6)$$

where g_h is the hydrostatic voltage coefficient and K is the dielectric constant in the poled direction.

In evaluating a candidate material for hydrophone application, it is important to define a 'figure of merit'. The figure of merit is useful when comparing different materials for the predefined application and also aids the simple intercomparison of the possible 'trade-offs' in different coefficients.

A useful figure of merit for the hydrophone materials is the product of the hydrostatic charge coefficient, d_h and the hydrostatic voltage coefficient, g_h [5]. The product $d_h g_h$ is given by :

$$d_h g_h = (d_{33} + 2d_{31})^2/\varepsilon_0 K \qquad (2.7)$$

and has the unit of m^2/N

Recently, an alternative hydrophone figure of merit was introduced taking into account the self-noise generated by the sensor material[6]. To minimize self-noise, the dielectric dissipation factor ($\tan\delta$) of the piezoelectric material should be as low as possible. Thus, the alternative figure of merit is expressed as $d_h g_h/\tan\delta$.

Another important consideration for hydrophone performance is the acoustic coupling between the hydrophone and its water environment. The acoustic impedance (Z) is defined by $Z = \rho c_L$, where ρ and c_L are material density and acoustic wave velocity in the material, respectively. The acoustic impedance of the transducer material should be close to that of water (1.5 Mrayls) in order to reduce the impedance mismatch at the hydrophone/water interface and ensure strong acoustic coupling. Since the characteristic acoustic impedance of a material is strongly dependent on its density, as well as for buoyancy considerations, the hydrophone material density should be as close to that of water as possible[7,8].

Finally, the properties of hydrophone should be independent of frequency, pressure, and temperature. Also, the hydrophone materials should possess a high degree of compliance so that it can conform to any surface shape and withstand mechanical shock[4].

2.2.2 Biomedical Imaging Applications

Biomedical imaging with ultrasonic (1-20 MHz) sound is widely used as a critical diagnostic tool which can produce real-time, high resolution of three dimensional images of internal soft body tissue without the use of potentially hazardous ionizing radiation.

The ultrasonic beam transmission capability of a transducer material can be characterized in part by its piezoelectric longitudinal charge coefficient (d_{33}). A transducer material's echo receiving sensitivity is directly related to its piezoelectric voltage coefficient (g_{33}). Large values of these coefficients are highly desirable and some researchers use the product of d_{33} and g_{33} as a figure of merit for pulse-echo transducers[7].

The dielectric constant is also important for the same reason it was for hydrophone applications. A K~100 permits a large g_{33} value and eases the electrical impedance matching between the transducer and the system instrumentation. The dielectric loss should also be minimized so as to prevent the loss of signal energy[9].

The thickness mode electromechanical coupling coefficient (k_t) is another value that indicates the energy conversion efficiency and potential sensitivity of a biomedical imaging transducer material. k_t is defined as the ratio of mechanical energy stored in a thickness mode transducer to the electrical energy supplied or vice versa[7]. For maximum efficiency, a thickness mode transducer should have a minimal planar mode coupling coefficient (k_p), so that the ratio k_t/k_p is as large as possible.

The mechanical quality factor (Q_m) is inversely proportional to the amount of mechanical loss due to internal friction within a transducer material. On one hand, a low Q_m implies that a material is mechanically lost and that signal energy is being wasted. On the other hand, a low Q_m is required to limit ringing, enabling the generation of short acoustic pulse lengths, thus offering improved axial resolution[9,10]. A Q_m~2-10 is a compromise value that limits ringing within the transducer without external damping layers[7].

The transducer's acoustic impedance should be near that of body tissue (1.5 Mrayls) for strong acoustic coupling, minimizing the reflection of acoustic signal at the transducer/skin interface. This would reduce the need for synthetic matching layer which is attached to the transducer surface to improve acoustic coupling with the body[10].

Finally, the transducer material should be compliant so that it may be easily shaped for focusing purposes and its processing should also be adaptable to mass production.

The optimum properties for these two applications are summarized in Table 2.1.

Table 2.1 Optimum transducer material properties for low and high frequency applications[7].

Property	Low Frequency (Hydrophone)	High Frequency (Biomedical imaging)
d_h (pC/N)	High	-
g_h (mVm/N)	High	-
d_{31} (pC/N)	Low	Low
d_{33} (pC/N)	High	High
g_{33} (mVm/N)	-	High
Dielectric Constant	~100	~100
tanδ	Low	Low
k_t	High	High
k_p	-	Low
Q_m	-	~2
Acoustic Impedance (Mrayls)	1.5	1.5
Density (g/cm^3)	~1.0	~1.0

2.3 Single Phase Piezoelectric Materials

Single phase piezoelectric materials can be classified either as ceramics or polymers. In the following sections. The charateristics of piezoceramics (Barium Titanate, Lead Zirconate Titanate, Lead Titanate and Lead Metaniobate) and the piezopolymer (Polyvinylidene Fluoride and P(VDF-TrFE) Copolymer) are discussed.

2.3.1 Ceramic Piezoelectric Materials

The high piezoelectric effect was discovered in the ferroelectric polycrystalline ceramics such as $BaTiO_3$, PZT, and other ceramic oxide compositions[3]. They are widely used in the various transducer applications but there are several disadvantages[4].

The hydrostatic charge coefficients ($d_h = d_{33} + 2d_{31}$) are small because d_{33} and d_{31} are opposite in sign and cancel on another. In addition, the relatively large dielectric constants of ceramics significantly reduce the piezoelectric voltage response. The high densities lead to large acoustic impedances, causing considerable signal loss at the ceramic-medium interface. Finally, the ceramics are brittle and cannot be easily fabricated into structures with large surface areas or complex shapes. The specific properties of several important piezoelectric ceramics will be described in the following subsections.

2.3.1.1 Barium Titanate

The d_{33} values of barium titanate ($BaTiO_3$) range from 85 pC/N for a single crystal, to 190 pC/N for a sintered ceramic, and to 280 pC/N for a sintered ceramic prepared from the asymmetrical barium titanate[11]. However, the d_h value (33 pC/N) of a sintered ceramic is relatively small due to its large d_{31} equal to -79 pC/N. Furthermore, the large dielectric constant (1700) of barium titanate results in the small piezoelectric voltage coefficients, g_{33} (13 mVm/N) and g_h (2 mVm/N)[12].

2.3.1.2 Lead Zirconate Titanate

Lead zirconate titanate [$Pb(Zr_xTi_{1-x})O_3$] is a solid solution consisting of two perovskite materials-tetragonal lead titanate ($PbTiO_3$) and rhombohedral lead zirconate ($PbZrO_3$)[3]. The properties of the PZT system largely depend on its composition. The optimum piezoelectric properties are found at compositions near its morphotropic phase boundary - ($Pb(Zr_{0.52}Ti_{0.48})O_3$), where both the tetragonal and rhombohedral phases coexist. For example, $Pb(Zr_{0.5}Ti_{0.5})O_3$ has d_{33} of 175 pC/N, and increases to 225 pC/N for $Pb(Zr_{0.52}Ti_{0.48})O_3$. Further increases have been obtained by the addition of dopants such as niobia, lanthanum oxide, magnesia, etc.[13].

Two representative types of PZT are denoted as 'hard PZT' and 'soft PZT'[14]. In hard PZT known as PZT-4, the Fe^{+3} ions are doped in Zr or Ti lattice sites and oxygen vacancies are created. It has low dielectric loss ($\tan\delta$ = 0.4%) and high mechanical quality factor (Q_m = 500) and is resistant to depoling due to the relatively high coercive field[7,12]. In soft PZT known as PZT-5, the Nb^{+5} ions are doped in Pb lattice sites and free electrons are liberated.

This material has moderate dielectric loss (tanδ = 2.0%) and low mechanical quality factor (Q_m = 80) due to the presence of free electrons. However, it has a relatively low coercive field and can be easily poled.

The PZT-5 is the most widely used piezoelectric material for the transducer applications primarily due to its high d_{33} (450 pC/N) coefficient and electromechanical coupling factor (k_t = ~0.5)[7,15]. But its d_h (40 pC/N) is relatively low and the high K (1800) leads to the low voltage coefficients, g_{33} (28 mVm/N) and g_h (2.5 mVm/N). In addition, the density of PZT (7.9 g/cm^3) is very high, which, in turn, increases the acoustic impedance (29 Mrayls).

2.3.1.3 Lead Titanate

The unique characteristic or $PbTiO_3$ compared to $BaTiO_3$ and PZT is its high structural anisotropy (c/a = 1.06). Because of this anisotropy, lead titanate is difficult to fabricate in bulk form. After sintering, as lead titanate cools below its curie temperature (T_c = 490

°C), it experiences a large spontaneous strain (~6%) due to a cubic to tetragonal phase transition. Causing it to crack and fracture. In order to improve the sintering characteristics and the electromechanical properties, lead titanate is modified with various dopants such as Ca, Sr, Ba, Sm, Co, and W[16-25].

Modified lead titanate ceramics are better suited for the transducer applications than most of other ceramic materials. One representative modified lead titanate that has been extensively investigated recently is $(Pb_{0.76}Ca_{0.24})((Co_{0.50}W_{0.50})_{0.04}Ti_{0.96})O_3$ with 2 mol% MnO added. $Pb(Co,W)O_3$ serves to lower the sintering temperature and inhibit grain growth, and MnO aids poling by increasing the resistivity of the ceramic[24,25]. The d_{33} (68 pC/N) is much larger than its d_{31} (-3 pC/N). As a result, its d_h (63 pC/N) is extremely large. Moreover, the low K (209) also permits the largest g_h (36 mVm/N) and d_hg_h figure of merit (2270×10^{-15} m^2/N) of all the piezoelectric ceramics.

In addition. Highly anisotropic electromechanical properties can be obtained in this material which favor its usage as a thickness resonance mode transducer. Its k_t (0.52) is very large, where as its planar coupling factor k_p

can be made vanishingly small (0.06). However, it has been reported that the modified lead titanate exhibits a significant variation of k_t, k_p and Q_m with temperature and the applied poling field[23,25].

2.3.1.4 Lead Metaniobate

Lead metaniobate ($PbNb_2O_6$) is the ferroelectric material with tungsten bronze crystal structure. Its promising properties for a piezoelectric ceramic transducer are its ability to withstand exposure to temperatures approaching its Curie point (570 °C) without severe depoling, its large d_{33}/d_{31} and k_t/k_p ratios, and low mechanical quality factor Q_m (24)[3,7,26]. The low Q_m is useful for the wideband ultrasonic transducers such as non-destructive testing and acoustical imaging. It has relatively low dielectric constant K (225) and large d_h (53 pC/N) and g_h (27 mVm/N) compared to $BaTiO_3$ and PZT.

However, lead metaniobate is difficult to fabricate in bulk form since it undergoes a large volume change upon cooling below its Curie point after sintering[3].

As a result, pure lead metaniobate bulk samples often fracture during fabrication. If not, microcracking usually results in sintered material with low strength and a large amount of porosity, which is reflected in its low Q_m value[27]. In order to produce dense ceramics, various additives were substituted - for example, Sr, Ba ions for Pb and Ta, Zr, Ti ions for Nb[26,28]. However, these additives also increase the dielectric constant, k_p and Q_m values, which is detrimental to the applications such as hydrophone and wide band ultrasonic transducer.

All references for properties quoted in the text are listed in Table 2.2.

Table 2.2 Electromechanical properties of ceramic piezoelectric materials.

Property	$BaTiO_3$	PZT-4	PZT-5	Modified $PbTiO_3$	$PbNb_2O_6$
d_{33} (pC/N)	190	289	450	68	85
d_{31} (pC/N)	-79	-123	-205	-3	-16
g_{33} (mVm/N)	13	26	28	37	43
d_h (pC/N)	33	43	40	63	53
g_h (mVm/N)	2	4	2.5	36	27
$d_h g_h$ (10^{-15} m^2/N)	65	170	100	2270	1430
K	1700	1300	1800	209	225
tanδ (%)	1.0	0.4	2.0	<2.0	0.6
k_p	0.35	0.62	0.63	0.06	0.07
k_t	0.38	0.51	0.49	0.52	0.32
Q_m	-	500	80	922	24
Ref.	11,12	7,12	7,15	25	7

2.3.2 Polymer Piezoelectric Materials

The piezoelectric activity of synthetic polymers is not as high as those found in the piezoceramics. However, the advantages of these materials as piezoelectric elements are in that they are tough, lightweight, and flexible, compared to the ceramic materials. They can be manufactured in the sheet form by a continuous roll process. They also offer a much higher dielectric strength than ceramics, along with a lower mechanical and acoustic impedance, making them very responsive sensors of mechanical signals[4]. Piezoelectric polymer films are currently used in many applications such as microphones, audio amplifiers, hydrophones, and sonar transducer, etc.. In the following subsections, the two most widely used piezopolymers will be discussed.

2.3.2.1 Polyvinylidene Fluoride (PVDF)

The discovery by Kawai in 1969 that PVDF could be poled to become piezoelectrically active opened the area of thin film piezopolymer applications[29].

PVDF is comprised of the chemical unit $(CH_2-CF_2)_n$ and its microstructure consists of polymer crystals within an amorphous matrix[30]. The volume fraction of crystalline material is typically 50-60%. Within crystallized polymer molecules, there is a noncentrosymmetric unit all which gives rise to a resultant dipole moment and associated piezoelectric activity.

PVDF polymer molecules are known to crystallize into four possible structures : α, β, γ, and tanδ[31]. In two of the crystal phases (α and β), the molecules align so that the dipole moments are parallel in the unit cell. However, the molecular chains of the α form pack to form an antipolar cell. The highest piezoelectric response is associated with the β form, which contains the maximum dipole moment. In order to produce the β phase, the α phase film is stretched to 3-5 times its original length to recrystallize the β-phase. The stretched film exhibits strong piezo- and pyroelectricity after poling[32].

PVDF has several advantages over the piezoelectric ceramic materials[4]. The thin film (typically 10-100 μm) is more sensitive to mechanical stress, withstands the higher voltage, and possesses a low density (1.8 g/cm³).

It is noted that d_{33} value of PVDF polymer has the negative sign; that is, the film thickness decreases when an electric filed is applied in the same direction as the poling field. This can be explained as follows: the applied electric field makes the dipole orientation more complete and the molecular packing more in order, causing the volume of film to decrease[31].

McGrath *et al.*[33] developed the thick PVDF films in excess of 1 mm thickness. Three classes of drawing were used in these films : voided, ultradrawn, and non-voided. The voided PVDF is drawn in a way that induces microcracking, making it more compliant than the ultradrawn and non-voided films. The ultradrawn PVDF is drawn at a much higher final draw ratio than the usual method. Non-voided PVDF is produced by drawing under the normal condition.

Voided material has the greatest hydrostatic piezoelectric coefficients and voltage sensitivities, which are ascribed to a low thickness compliance and low dielectric constant. The figure of merit, $d_h g_h$ for this material is an order of magnitude higher than non-voided PVDF.

Recently, Scheinbeim *et al.*[34] developed a new processing method for the preparation of piezoelectric PVDF films. The process comprises dissolving PVDF in a suitable solvent such as tricresylphosphate. The mixture is placed in a vacuum oven, and then poled under the appropriate temperature at which the solvent is evaporated. In this way, PVDF film with desired shape can be fabricated without mechanical stretching, and at the same time, poling can be performed efficiently. Values of d_{31} of 13 pC/N, d_{33} of -32 pC/N, and K of 31 have been reported which are promising compared to those of PVDF films prepared by the conventional drawing and poling method.

The piezoelectric behavior of PVDF film under dynamic pressure has been studied[35]. It has been found that the piezoelectric activity of PVDF is practically reversible up to 9 kbar. This suggests that PVDF can be also used as the dynamic pressure transducers.

Compared to the piezoceramics, it can be seen that PVDF has relatively low piezoelectric charge coefficients and high voltage coefficients due to a small dielectric constant. This indicates that PVDF is better acoustic receiver than transmitter, whereas piezoceramics are better suited for the opposite. However, the low dielectric constant of PVDF makes electrical impedance mismatching more complicated by necesstiating the use of amplifiers in close proximity to the transducer elements[4].

Other limitations of PVDF include its low electromechanical coupling factor (k_t = ~0.2), high required poling field and limited tolerance to the elevated temperatures[7,36]. A very high electric field (~1 MV/cm) is necessary to pole PVDF, which limits the thickness of the sample. Furthermore, PVDF irreversibly loses its piezoelectric activity at temperatures above 130 °C.

2.3.2.2 P(VDF-TrFE) Copolymer

Recently, copolymers consisting of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) have been developed[25]. Since these copolymers contain a greater porting of the fluorine atoms than PVDF, their molecular chains cannot accommodate the chain conformation of the α-phase and crystallize spontaneously into the polar β phase. In addition, a reduced poling field (< ~1 MV/cm) can be used in these copolymers.

The piezoelectric properties of the copolymer have been measured for a wide composition range[25,37-40]. The piezoelectric charge coefficient, d_{31} increases and attains its maximum (32 pC/N) at about 55 mol% VDF; it becomes small (7-15 pC/N) in the VDF range of 65-82 mol%, and again increases to 20 pC/N at higher VDF content. On the other hand, the electromechanical coupling factor, k_t is small (0.01-0.1) for the range below 55 mol% VDF, but it becomes very large (0.27-0.32) in the VDF range of 65-82 mol% . To achieve such a high k_t value, it has been found necessary to increase the crystallinity of copolymer by annealing prior to or during poling treatment at temperatures above T_c. The copolymer of 60 mol% VDF exhibits significantly higher figure of merit, $d_h g_h$ than that of PVDF. The copolymer of 75 mol% VDF shows the very large g_{33} (380 mVm/N) and a large k_t (0.3) compared to PVDF.

2.4. Piezoelectric Ceramic-Polymer Composites

From the previous sections, it can be seen that no known single phase piezoelectric material meets the various conflicting requirements for transducer applications. A new piezoelectric material consisting of ceramic and polymer phases was developed in a composite form, which potentially allows a combination of electromechanical properties unattainable in the single phase piezoceramics or polymers[41-74]. The polymer phase in a composite imparts flexibility and decreases the density and dielectric constant, while the ceramic phase gives rise to the piezoelectricity. These effects will then lower the acoustic impedance and enhance the piezoelectric voltage coefficient of the composite.

The piezoelectric ceramic-polymer composites were initially intended for underwater hydrophone applications. It has been demonstrated that certain composite hydrophone materials are much more sensitive than PZT ceramics while satisfying other requirements[4]. More recently, the concept of composite material has been extended to other applications such as an ultrasonic transducer for acoustic imaging and sound absorbers.

These composites are a kind of smart materials that can respond passively in a useful manner by tailoring the composite structures in which each phase is connected[41]. The connectivity patterns and several types of piezocomposites will be described in the following subsections.

2.4.1 Phase connectivity

In a ceramic-polymer composite, the arrangement of the individual phases within a composite is important for the electromechanical properties of the composite. Newnham *et al.*[51,60] developed the concept of connectivity to describe the manner in which the individual phases are interconnected.

Each phase in composite may be self-connected in zero, one, two, or three dimensions. In a diphasic system, there are ten different types of connectivities: 0-0, 1-0, 2-0, 3-0, 1-1, 2-1, 3-1, 2-2, 2-3 and 3-3. These connectivities are illustrated in Figure 2.2 using a cube as the basic building block. The first digit refers to the piezoelectrically active ceramic phase, and the second one to the polymer phase. Figure 2.3 represents the schematic diagram of different piezoelectric ceramic-polymer composites. All these composites showed improved

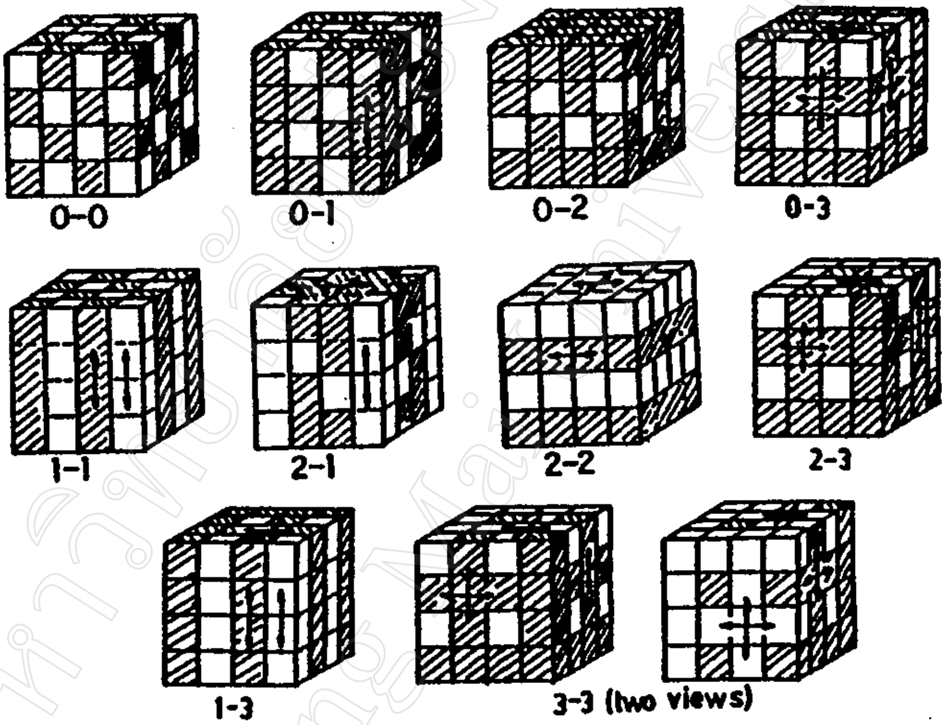

Figure 2.2 Ten different connectivity patterns of diphasic Materials[60].

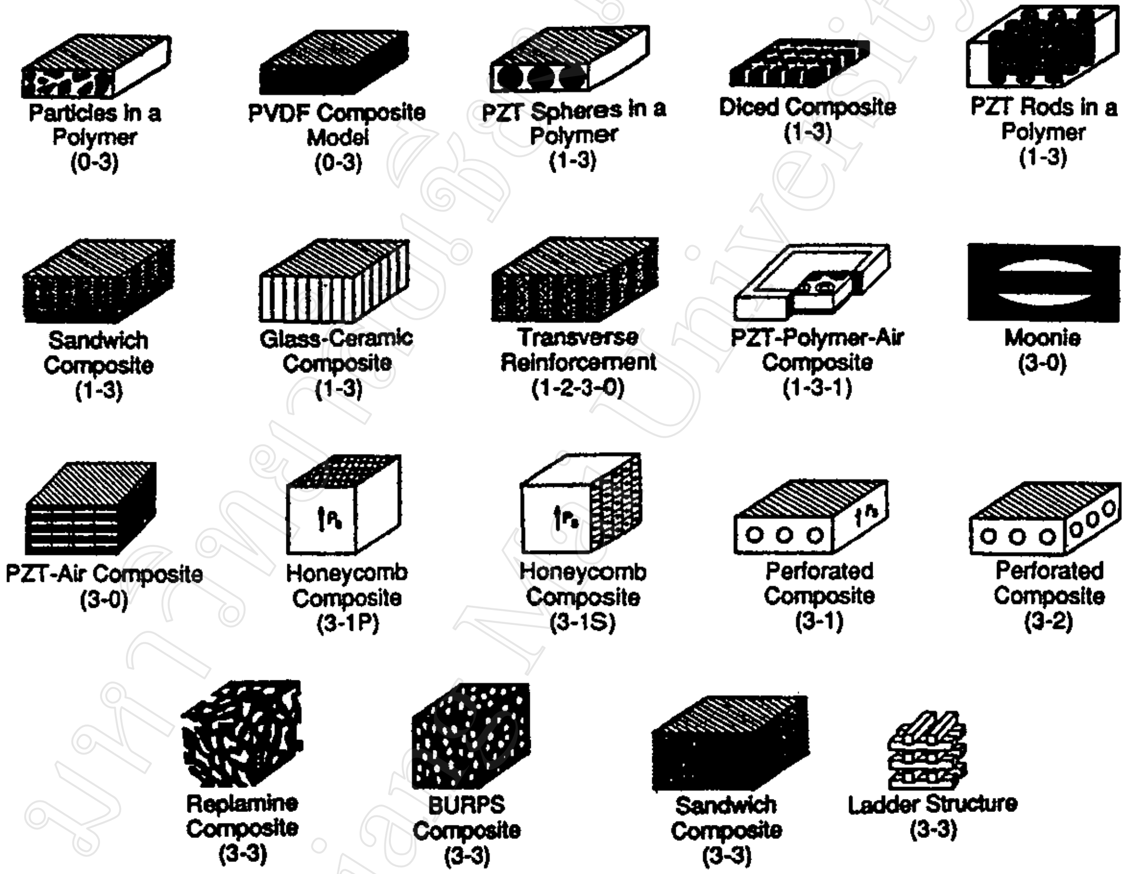

Figure 2.3 Schematic diagram of various piezoelectric ceramic-polymer composites.

piezoelectric properties compared to single phase piezoelectric cermaics.

Among the many different types of composites, the piezocomposites with 3-3, 1-3, and 0-3 connectivity have been extensively investigated. These are reviewed in the following sections with more detailed description on the 0-3 type composite.

2.4.2 Piezocomposites with 3-3 Connectivity

In a composite with 3-3 connectivity, each component phase is three-dimensionally self-connected in intimate contact with each other. Since the piezoelectric phase is continuous between electrodes with this connectivity, this composite can be efficiently poled[4].

In the first fabrication of this type of composite called 'replamine composite', the naturally available coral was used as the initial template material[42]. The coral is first vacuum impregnated with casting wax. Hydrochloric acid is used to leach away the calcium carbonate coral skeleton. The wax negative is then filled with a slip consisting of PZT powder. Afterwards, the wax is carefully burned away at low temperature and the PZT is sintered. Finally, the porous PZT network is vacuum backfilled with silicon elastomer to form a composite. d_{33} of 160 pC/N and d_hg_h of 5040×10^{-15} m^2/N are reported for this composite, which is about fifty times larger than that of PZT ceramic.

However, the hydrostatic properties of replamine composite are found to degrade after few times of cycling the pressure up to 90 psi[55]. In addition the production of replamine composites is industrially unfavorable since it requires a naturally occuring biological material. Also, there are problems with composite reproducibility.

An improved fabrication method for 3-3 composites was reported by Shrout, *et al.*[43]. These composites are called 'BURPS', an acronym for BURned out Plastic Spheres. The processing involves mixing PZT powder with an organic binder and polymethyl-methacrylate (PMMA) spheres, 50-150 μm in diameter, and pressing the mixture into pellets. The volatile spheres and binder are removed upon sintering and porous PZT skeleton is formed. After backfilling with a polymer material, BURPS composites are formed. The composites composed of PZT (50 vol%) and silicon rubber exhibited the d_{33} of 200 pC/N and d_hg_h of 8100×10^{-15} m^2/N. which is even larger than those of the replamine composite.

However, this composites also has problems associated with the reproducibility and the hysteresis effects of d_hg_h with the application of hydrostatic pressure[44].

2.4.3 Piezocomposites with 1-3 Connectivity

In piezocomposites possessing 1-3 connectivity, the piezoelectric ceramic phase is in the form of rods, fibers, or pillars and the polymer matrix phase is three dimensionally self-connected. The 1-3 composites have excellent hydrostatic sensitivity. The large d_{33} value is obtained due to the parallel connection of piezoceramics, whereas the d_{31} value is reduced because of series connection in the lateral dimension where the mechanical load is absorbed by the polymer and not transferred to the PZT rods. Finally the dielectric constant is minimized because of the large volume of polymer (70-95 vol%)[10,41].

Initially, 1-3 type piezocomposites were prepared using PZT rods that were extruded, sintered, and hot-pressed[54]. A fixture was used to align the rods in parallel. After backfilling with polymer, cutting perpendicular to the rod direction completes the composite fabrication. The problem with this processing is that it is extremely time consuming.

A simplified fabrication procedure was developed by Savakus, et al., called 'dice and fill' method[45]. In the process, the sintered ceramic body is cut to form deep grooves using a dicing saw. An array of square pillars are formed being held in place by its connected base. The grooves are backfilled with polymer and the base is removed by either grinding or cutting. An improved version of this method was attempted by capping the top and bottom surfaces with a thick brass or stainless steel electrode and encapsulation the sides with alumina plates[4]. Capping serves to distribute the longitudinal components of the hydrostatic stress more uniformly over the PZT pillars, while transverse stress components are supported by alumina and $d_h g_h$ (20000×10^{-15} m^2/N) were reported in this composite.

The 1-3 piezocomposites have also been extensively investigated for their use in ultrasonic applications such as biomedical imaging. For this application, the properties of 1-3 composites are far superior to all other known piezocomposites[7]. They have low acoustic impedance (8.5 MRayls). And high g_{33} (100 mVm/N) as well as large K (300) and d_{33} (290 pC/N). The most important feature of these composites is its extremely large k_t (0.75). Also, the soft polymer phase prevents coupling of undesirable lateral acoustic vibrations. This reduces the k_p and improves the k_t/k_p ratio.

However, there are many variables that determine the properties of 1-3 composite. These include the type of polymer material, PZT vol%, pillar size and aspect ratio, and the spacing between pillars[9,10]. Fine scale of PZT distribution enables composite properties to be more homogeneous across the entire electrode area. A fine scale also permits the use of a softer polymer matrix material for optimum piezoelectric properties without lateral resonant wave interference. This is particularly important at higher operating frequencies such as those utilized in biomedical imaging[10]. However, the fine scale distribution is difficult to achieve using the usual dice and fill technique.

A new fabrication method call 'relic processing' has been developed by Safari, *et al.*[46,47]. This processing uses carbon fiber as a starting material. The woven carbon fiber is impregnated with PZT precursor after soaking in a PZT stock solution. The subsequent heat treatment removes the carbon leaving a PZT fiber relic with the same shape as the original woven fiber template. After sintering, relics were backfilled with polymer to form composites. Preliminary results showed the promising values of d_{33} (143 pC/N) and $d_h g_h$ (3000×10^{-15} m^2/N). This work is underway to further optimize the processing steps and improve the electromechanical properties of composites.

2.4.4 Piezocomposites with 0-3 Connectivity

Composites with 0-3 connectivity consist of a particulate ceramic phase distributed within a three dimensionally connected polymer phase [Figure 2.4].

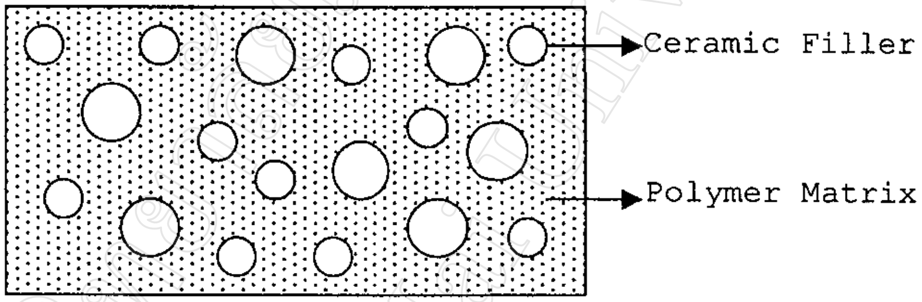

Figure 2.4 Schematic diagram of 0-3 ceramic-polymer composite.

This microstructure is similar to that of PVDF polymer in which a crystalline phase is distributed in an amorphous matrix[58].

When compared to other types of composites, the most attractive advantages of the 0-3 composite is its ease of fabrication in variety of forms, including thin sheets. Extruded rods and fibers, and certain molded shapes. This type of composite is also amenable to mass production and can be made flexible to conform to the curved surfaces[4].

Although 0-3 composites appear to be simple in structure, their properties are strongly dependent on both the piezoelectric ceramic and polymer phases as well as the fabrication methods employed. The basic principle of designing a 0-3 ceramic-polymer composite system for hydrophone applications entails achieving the d_{33} as large as possible while reducing the d_{31} for an increased $d_h g_h$ figure of merit.

Many different variations have been attempted to optimize these factors to make improved 0-3 composites, primarily involving the choice of ceramic filler materials and the composite fabrication methods. In the following subsections, the poling behavior of 0-3 composite and its development achieved by employing the different types of ceramic fillers and composite fabrication methods will be described.

2.4.4.1 Poling of 0-3 Composite

Since in a 0-3 composite, the piezoelectric ceramic particles are isolated in the polymer matrix. Poling is more difficult than in other types of composites. The poling behavior of 0-3 composite will be considered in the following discussion.

For a 0-3 composite consisting of the spherical grains embeded in a matrix, the electrical field E_1 acting on an isolated spherical grain is given by[75],

$$E_1 = 3K_2E_0 / (K_1+3K_2) \qquad (2.8)$$

In this equation, K_1 and K_2 are the dielectric constants of the spherical piezoelectric grains and the polymer matrix, respectively, and E_0 is the externally applied electric field. For example, in the 0-3 composite of PZT powder and epoxy polymer, $K_1 \sim 1800$ and $K_2 \sim 5$. When an external field of 100 kv/cm is applied to such a composite, the electric field action on the piezoelectric particles is only about 1 kv/cm which is insufficient to pole PZT. According to the above equation, $E_1 \sim E_0$ only when the dielectric constant of the piezoelectric phase approaches that of the polymer phase. Since most of the ferroelectric ceramic materials have very high dielectric constants compared to those of polymer materials, the above condition cannot be satisfied.

On the other hand, the importance of electrical conductivity to poling can be considered by applying the Maxwell-Wagner model to 0-3 composite[75]. This model explains a relationship between the electric fields and the conductivities of the two phases.

A 0-3 composites with alternating piezoelectric ceramic grains and the polymer between the two electrodes can be approximated by a two-layer model, as shown in Figure 2.5. The conductivity and effective thickness of the ceramic and polymer are σ_1 and d_1, and σ_2, and d_2 respectively.

When a DC poling voltage is applied for a period longer than the sample relaxation time, the ration of the electric field, E_1 on the ceramic phase 1 to the electric field E_2 applied to the polymer phase 2 is given by,

$$E_1/E_2 = \sigma_2/\sigma_1 \tag{2.9}$$

This ratio is also small unless the conductivity of the polymer phase (σ_2) is greater than that of the ceramic phase (σ_1) or the effective thickness of polymer (d_2) is far less than that of the ceramic (d_1).

However, since the most ceramic materials have higher electrical conductivities [10^{-11}-10^{-10} (ohm-cm)$^{-1}$] compared to those of polymer materials [10^{-17}-10^{-13}(ohm-cm)$^{-1}$], the above condition cannot be satisfied, usually making poling the 0-3 composites difficult[76].

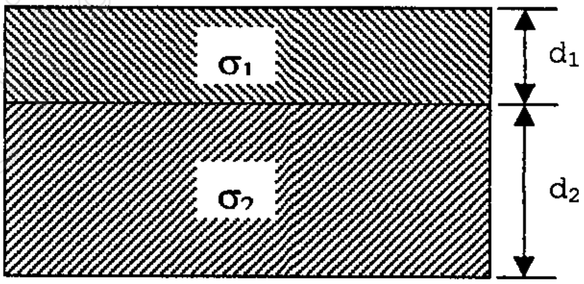

Figure 2.5 Maxwell-Wagner two-layer capacitor.

2.4.4.2 Composite Processing and Fabrication

Many methods were used to fabricate the 0-3 piezoelectric composites. The simplest one, conventional method, is the mixing of ceramic powder in a polymer matrix on a calender. In 1979, Furugawa *et al.*[77] used this method to study properties of the PZT-polymer composite. This can make ceramic loading about 50 vol%. Most of research studies to date used the solid loadings of 60-70 vol% to achieve the useful piezoelectric properties[4]. Many methods were studied in this aspect.

A new one was developed to make "fired 0-3 composites"[78-80]. In this process, the piezoelectric filler loading of 60-70 vol% could be attained. The fired 0-3 composite composed of lead titanate and epoxy resin exhibited a large d_{33} coefficient (70 pC/N), however, its $d_h g_h$ figure of merit was reported to be relatively low ($1750 \times 10^{-15} m^2/N$). Furthermore, there is a portion of 3-3 connectivity present within these composites. The improvement in the properties is partly due to the 3-3 connectivity.

A different fabrication method was developed to make the thin film 0-3 composites for the potential use in large area sensor applications[81-83]. The basic idea was to prepare a piezoeletric paint by replacing the pigment with a piezoelectric ceramic filler. In the process, an acrylic copolymer and a polyurethane were loaded with 60-70 vol% PZT or $PbTiO_3$.

Next method is colliodial processing[84]. It can make ceramic loading up to 70 vol% and give high value of piezoelectricity. Another important method that was studied by Fries and Moulson[85] in 1994 is the tape casting method. It can make ceramic loading over 60 vol%.

Among these methods, other ways to improve piezoelectric properties are surface treatment of particles of filler ceramic which were studied in 1997 by Xuemei *et al.*[86]. Furthermore, the poling quality was improved by Safari[76] in 1986 by adding semiconductor phase in the composite. However, it was observed that the addition phase also increased the dielectric dissipation factor (0.08) of the composite.

2.5. Summary

The piezoelectric and physical properties of single phase piezoceramics or polymer do not successfully meet the various requirements of the transducer application such as hydrophone and ultrasonic imaging. Piezoelectric ceramics and polymer have properties that are at opposite extreme. Piezoceramics such as PZT typically have a large dielectric constant and piezoelectric charge (d_{33}) coefficient, but relatively small voltage (g_{33} and g_h) coefficients. They are also brittle and have high densities. Piezopolymer, on the other hand, are tough, lightweight and flexible. But they have low piezoelectric charge (d_{33} and d_h) coefficients. Also, due to a low dielectric constant of piezopolymer, the amplifier needs to be incorporated to overcome the noise problems.

By combining these single phase materials into a composite form, it is possible to achieve the desirable properties of a transducer by minimizing their detrimental properties. Flexible piezoelectric composites have evolved with various connectivities by which each component phase is arranged, allowing the composite properties to fit the needs of specific applications.

Some critical electromechanical properties such as d_h, g_h, g_{33} and k_t have been much improved in certain types of composites, particularly those with 3-3 and 1-3 connectivities. The composites with 0-3 connectivity also exhibit a relatively large g_{33}, g_h and d_hg_h figure of merit over those of single phase materials. In addition, the 0-3 composites are highly desirable because of their ease of fabrication, which is able proceed to mass production.

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