

CHAPTER 2

THEORY AND LITERATURE SURVEY

2.1 Piezoelectricity

In the 1880s, Pierre and Jacques Curie discovered that some crystalline materials, when compressed, produced a voltage proportional to the applied pressure and that when an electric field is applied across the material, there is a corresponding change of shape. This characteristic is called piezoelectricity or pressure electricity (Piezo is the Greek word for pressure).

Two effects are operative in piezoelectric crystals, in general, and in ferroelectric ceramics, in particular. The direct effect (designated as a generator) is identified with the phenomenon whereby electrical charge (polarization) is generated from a mechanical stress, whereas the converse effect (designated as a motor) is associated with the mechanical movement generated by the application of an electrical field. Both of these effects are illustrated in Figure 2.1.

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 change 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 [12].

Of 32 crystal classes, 11 are centrosymmetric and consequently cannot exhibit polar properties [13]. 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.

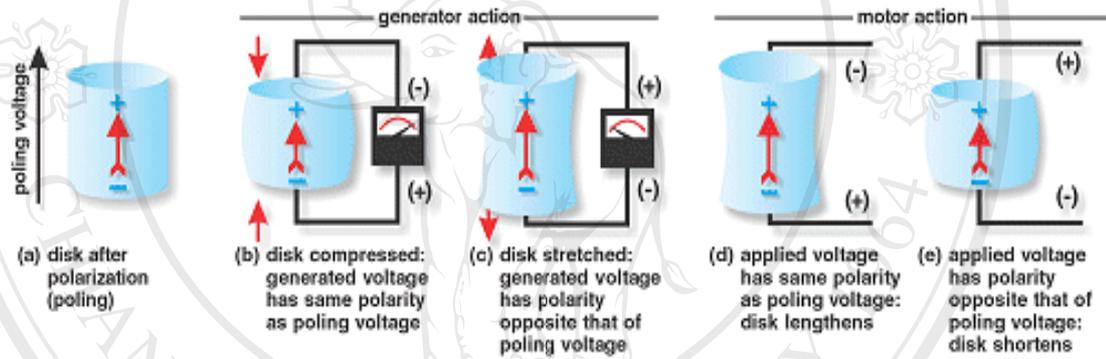


Figure 2.1 Piezoelectric effects in ferroelectric ceramics [14].

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 change initiated by the application of an electrical field.

The direct piezoelectric effect is described using the matrix notation,

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

$$i = 1,2,3$$

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

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:

$$\begin{aligned} \varepsilon_{ij} &= d_{ij}E_i \\ i &= 1,2,3 \\ j &= 1,2,3,4,5,6 \end{aligned} \quad (2.2)$$

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

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

$$\begin{aligned} E_i &= g_{ij}\sigma_j \\ i &= 1,2,3 \\ j &= 1,2,3,4,5,6 \end{aligned} \quad (2.3)$$

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:

$$\begin{aligned} g_{ij} &= d_{ij}/\varepsilon_{ii}\varepsilon_0 \\ i &= 1,2,3 \\ j &= 1,2,3,4,5,6 \end{aligned} \quad (2.4)$$

where, ϵ_{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 [13]. 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} [13,15]. Also, when a charge is applied and crosses a piezoelectric material, it will elongate in the poled 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 2.2]

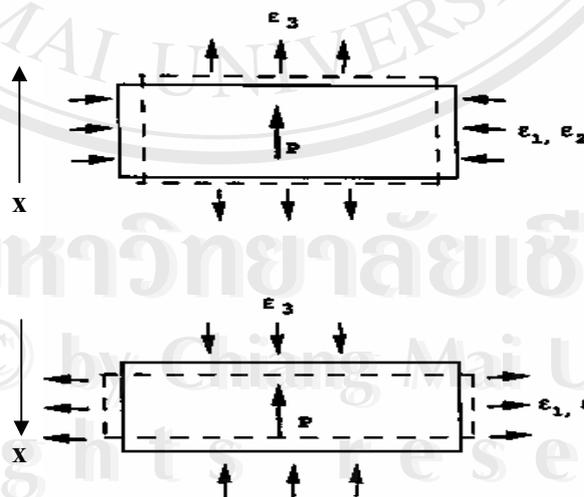


Figure 2.2 Schematic representation of piezoelectric response under the electric field E.

Possibly the best single measurement of the strength of a piezoelectric effect is the electromechanical coupling factor k . When an electric field is applied, it measures the fraction of the electrical energy converted to mechanical energy (or vice versa when a crystal or ceramic is stressed). The actual relationship is in terms of k^2 :

$$k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}}$$

or

$$k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}}$$

Since the conversion of mechanical to electric energy is always incomplete, k^2 is always < 1 , and thus k is also < 1 . Typical values of k are 0.10 for quartz, 0.4 for barium titanate ceramic, 0.5-0.7 for $\text{Pb}(\text{Ti,Zr})\text{O}_3$ ceramic, and as much as 0.9 for Rochelle salt at its 24 °C Curie point.

2.2 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 ($\text{K}_x\text{Na}_{1-x}\text{NbO}_3$) and Potassium Tantalate Niobate ($\text{K}(\text{Ta}_x\text{Nb}_{1-x})\text{O}_3$) have a perovskite type structure.

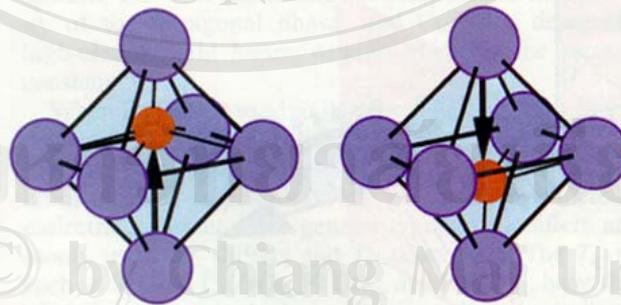
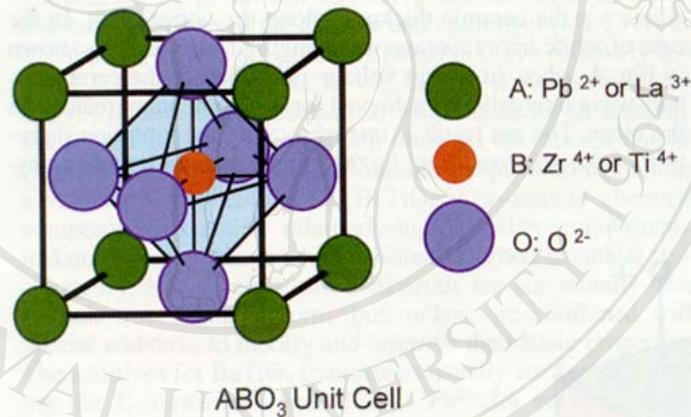


Figure 2.3 The unit cell and ABO_3 perovskite structure of PZT [15].

2.3 Single Phase Piezoelectric Materials

Single phase piezoelectric materials can be classified either as ceramics or polymers. In the following sections. The characteristics 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 BaTiO₃, PZT, and other ceramic oxide compositions. They are widely used in the various transducer applications but there are several disadvantages [16].

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 Lead Zirconate Titanate

Lead Zirconate Titanate (PZT) is a binary solid solution of PbZrO_3 , an antiferroelectric (orthorhombic structure) and PbTiO_3 , a ferroelectric (tetragonal perovskite structure). PZT has a perovskite type structure with the Ti^{4+} and Zr^{4+} ions occupying the B site at random. At high temperatures PZT has the cubic perovskite structure which is paraelectric. On cooling below the Curie point line, the structure undergoes a phase transition to form a ferroelectric tetragonal or rhombohedral phase. In the tetragonal phase, the spontaneous polarization along the $\langle 100 \rangle$ set of directions while in the rhombohedral phase the polarization is along the $\langle 111 \rangle$ set of directions. Most physical properties such as dielectric and piezoelectric constants show an anomalous behavior at the morphotropic phase boundary (MPB). The MPB separating the two ferroelectric tetragonal and orthorhombic phases has a room temperature composition with a Zr/Ti ratio of $\sim 52/48$. PZT ceramics with the MPB composition show excellent piezoelectric properties. For example, $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ has d_{33} of 175 pC/N, and increases to 225 pC/N for $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$. Further increases have been obtained by the addition of dopants such as niobia, lanthanum oxide, magnesia, etc.[16-17].

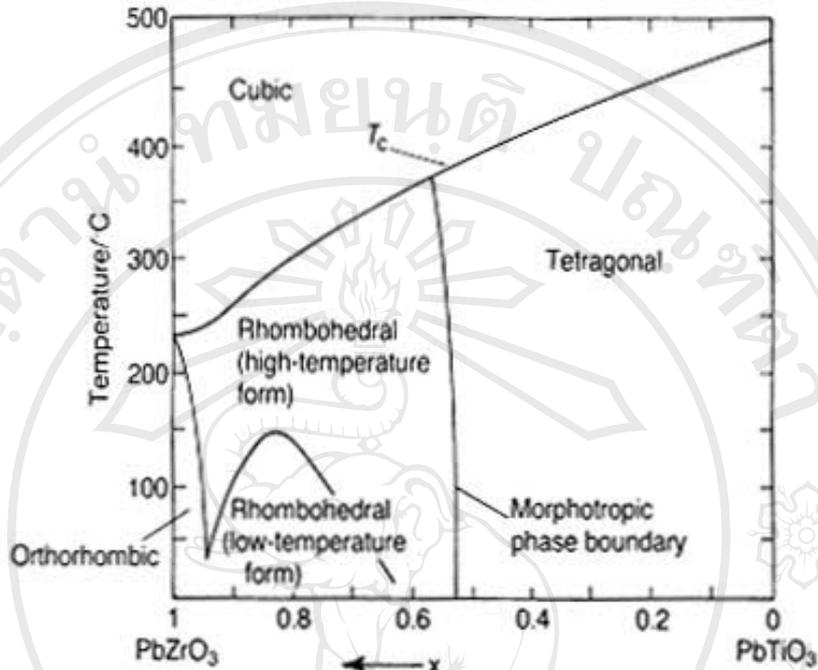


Figure 2.4 The phase diagram of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ [18].

Two representative types of PZT are denoted as ‘hard PZT’ and ‘soft PZT’[19].

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 [20,21]. 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 ($\tan\delta = 2.0\%$) 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 ($k_t = \sim 0.5$) [20,22]. But its d_h (40 pC/N) is relatively low and the high ϵ_r (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).

Since the PZT shows the outstanding piezoelectric properties, many groups of researcher [23-43] tried to develop its properties. Modifying the fabrication of PZT powder as well as preparation route have been employed.

In 1981, Goo *et al.* [23] used the transmission electron microscope (TEM) studied the $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ with 3 wt% of excess lead oxide and found that the grain boundary of PZT showed the amorphous phase of 10 nm thick, with the quantity of Pb located at the grain boundary higher than that in the grains.

Cho and Bigger [24] examined the $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ powder prepared by from the conventional mixed oxide method and molten salt by using SEM technique. They reported that the particle size obtained from mixed oxide route was found to depend on the calcining temperature. On the contrary, the powder prepared from molten salt technique showed opposite trend, however, the powder showed higher homogeneity and density.

Lal *et al.* [25] fabricated $\text{Pb}_{0.94}\text{Sr}_{0.06}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ powder by spray dry technique and the conventional mixed oxide method. The samples were sintered at temperature 1000-1250 °C for 0.5-12 hr. The density of 97% (compare with theoretical

density) obtained from sample sintered at 1000 °C and 1300 °C for sprayed samples and mixed oxide samples, respectively. Moreover, dielectric constant, piezoelectric coefficient and planar coupling factor of ceramic were increased when grain size was larger and the decreasing of these values obtained when the porosity was higher.

In 1994, Tunkasiri [26] prepared fine powder of PZT from chemical route. MnO_2 was used for doping. $\text{B}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-CdO}$ was added to reduce the sintering temperature. The results showed that the sintering temperature was found to reduce from 1250 °C to 1000 °C. Furthermore, PbO phase was not found at this temperature. Aungkavattana *et al.* [27], in 1995, fabricated the thin films of PZT by sol-gel method which the platinumized Si and (100) Mg were used as substrates. Films were annealed with the rate of 50 °C/min and 100 °C/min. The secondary phase was still found at temperature 595-600 °C indicating that rate of annealing could not remove the formation of second phase. In the same year, Kolb *et al.* [28] found that the width of morphotropic phase boundary increased with decreasing of sintering temperature and increasing of concentration of dopant.

Boudaren *et al.* [29] employed thermal analysis, XRD and chemical techniques to examine the PZT powder prepared from the oxides of Pb_3O_4 , TiO_2 and ZrO_2 with the dopants: NiO, Fe_2O_3 and Ta_2O_5 . They found Pb_3O_4 phase at 240 °C and 390 °C and the PZT phase at 650 °C with no impurity. In the same year, Jim *et al.* [30] investigated the dielectric properties of PZT ($\text{Zr/Ti} = 52/48$) prepared by mixed oxide method and found that the maximum dielectric constant would be decreased with the decreasing of grain size and phase transformation temperature (from cubic to tetragonal) would be increased.

The lattice parameter of tetragonal system were $a = 4.0395 \text{ \AA}$ and $c = 4.143 \text{ \AA}$. Furthermore, Chakrabarty and Maiti [31] fabricated PZT from gel of citrate-nitrate and activated by heat for oxidation-reduction. The fine and homogeneous particle with no fluctuation could be obtained. The obtained particle size was about 1.1 \mu m and 0.16 \mu m measured by using Sedigraph and surface area, respectively. Moreover, the tetragonal phase changed to rhombohedral phase when the mole percent of Zr was increased to 54%.

In 1998, Das and Pramanik [32] prepared the fine powder of PZT with the ratio of $\text{Zr/Ti} = 60/40$ by hydrothermal technique. The solution of Diethanolamine (DEA) and hydratemetaloxide of Ti(iv), Zr(iv) and Pb(ii) ions were used as precursors. They found that the single phase obtained at temperature $220 \text{ }^\circ\text{C}$ and $500 \text{ }^\circ\text{C}$ for 5 hr and the average particle size were 190 and 480 nm, respectively. In the same year, Law *et al.* [33] studied the effect of pyrolysis temperature (300 and $600 \text{ }^\circ\text{C}$) on PZT films prepared by sol-gel technique and found that [111] changed to [100] when temperature is higher than $400 \text{ }^\circ\text{C}$. Moreover, the increasing of remanent polarization (P_r) was obtained with longer annealing time. Furthermore, the single phase of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ prepared from co-precipitation technique was obtained at temperature $500 \text{ }^\circ\text{C}$. High density with homogeneous grain were obtained at $1200 \text{ }^\circ\text{C}$ [34].

In 1999, Tanasoiu *et al.* [35] studied the effect of Niobium and Lithium dopants on the structure and piezoelectric properties of $\text{Pb}(\text{Zr}_{0.051}\text{Nb}_3\text{Li})_x\text{Ti}_{0.49-x}\text{O}_3$ when x was in the range of 0.015 - 0.050 and sintered at 1200 - $1300 \text{ }^\circ\text{C}$ for 4 hr. They found that the optimize piezoelectric properties was obtained when $x = 0.020$, the dielectric constant,

planar electromechanical coupling factor (k_p) and mechanical coupling factor (Q_m) were 1700, 0.59 and 75, respectively. In the same time, Hayashi *et al.* [36] fabricated PZT powder by adding $Pb_5Ge_3O_{11}$ (PGO) for sintering aid. The PZT powders with size of 150 nm were coated with PGO which prepared from the solutions of $Ge(OiPr)_4$ and $Pb(NO_3)_2$ by sol-gel method. 1 wt% of PGO was added into PZT powder. Heating was done at 750 °C for 2 hr. The density of the ceramic was found to be 95% of the theoretical density. Moreover, the PGO could reduce the sintering temperature from 1050 °C down to 750 °C and the electromechanical coupling factor was 0.56.

For the next year, Corker *et al.* [37] tried to reduce sintering temperature of PZT by adding Cu_2O and PbO as the sintering aids. It was found that ceramics sintered at 800 °C showed high density when compared with conventional ceramics which sintered at higher temperature (1260 °C). Moreover, the nanocrystalline of PZT was prepared by Das *et al.* [38]. The Ti(IV), Zr(IV), Pb(II) ions, organic acid and amines were used as precursors. The different of complexing agents such as oxalic acid, tartaric acid, theylene diamine tetra acetic acid (EDTA), diethanolamine (DEA) were used for mixing with the samples prior to sintering. Study of the effect on particle size and dielectric properties of PZT. It could be seen that the precursors which obtained from mixing of Ti(IV)-Zr(IV)-X/Pb(II-EDTA) (when x = oxalic acid and tartaric acid) and Ti(IV)-Zr(IV)-Pb(II)-Y (Y = diethanolamine) solutions could be prepared the single phase of PZT as temperature at 600, 400 and 200 °C, respectively. And the corresponding average particle size were about 60, 30 and 25 nm, respectively. Kong *et al.* [39] used the high-energy ball milling for preparing the fine powder of $Pb(Zr_{0.52}Ti_{0.48})O_3$ from PbO , TiO_2 , and ZrO_2 . The XRD

and Raman spectra showed the PZT phase after milling for 20 hr with the grain size about 10 nm. Besides, the problems from the volatile element (Pb and Bi) could be avoided by using this method. Wu *et al.* [40] prepared PZT (52/48) from sol-gel method and found the single phase of PZT after annealing temperature at 600 °C for 1 hr and ceramic with density of 96% (of the theoretical density) obtained when sintered with temperature 950-970 °C for 2 hr. The dielectric constant, piezoelectric coefficient, remanent polarization and coercive field of PZT ceramics were 1000, 135 pC/N, 20 $\mu\text{C}/\text{cm}^2$ and 10.6 kV/cm, respectively.

Qiu and Hong [41] studied the effect on electrical properties of $\text{Pb}(\text{Y}_{1/2}\text{Nb}_{1/2})(\text{PYN})$ doped $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ and found that the remanent polarization of PZT was higher with the increasing of PYN content and the maximum value was 43.679 $\mu\text{C}/\text{cm}$ when 1.5 mol% of PYN was added. Li *et al.* [42] prepared thin film of PZT from sol-gel technique with thickness of 40 nm – 2.4 μm . The LaAlO_3 was used as substrate and the inorganic zirconium was used as precursor. They found that perovskite phase obtained after annealing at temperature 680 °C. Moreover, the thicker film showed the higher epitaxy and density.

Furthermore, Nasor *et al.* [43] prepared mixture of PZT with different concentration of SrO and found that remanent polarzation, coercive field and planar coupling factor were 6.9-8.9 $\mu\text{C}/\text{cm}^2$, 6.6-7.8 kV/cm and 0.45-0.53, respectively.

2.3.1.2 Lead Titanate

The unique characteristic of PbTiO_3 compared to that of 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 ($T_c = 490^\circ\text{C}$), 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 [44-53].

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 $(\text{Pb}_{0.76}\text{Ca}_{0.24})((\text{Co}_{0.50}\text{W}_{0.50})_{0.04}\text{Ti}_{0.96})\text{O}_3$ with 2 mol% MnO added. $\text{Pb}(\text{Co},\text{W})\text{O}_3$ serves to lower the sintering temperature and inhibit grain growth, and MnO aids poling by increasing the resistivity of the ceramic [52,53]. 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 $d_h g_h$ figure of merit ($2270 \times 10^{-15} \text{ m}^2/\text{N}$) 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 [51,53].

2.3.1.3 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) [16,20,54]. 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 ϵ (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 [16]. 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 [18]. In order to produce dense ceramics, various additives were substituted – for examples, Sr, Ba ions for Pb and Ta, Zr, Ti ions for Nb [54,55]. 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 2.1.

Table 2.1 Electromechanical properties of ceramic piezoelectric materials.

Property	BaTiO ₃	PZT-4	PZT-5	Modified PbTiO ₃	PbNb ₂ O 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
ϵ_r	1700	1300	1800	209	225
$\tan \delta$ (%)	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.	56,57	20,57	20,22	53	20

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 [56]. 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 [57].

PVDF is comprised of the chemical unit $(\text{CH}_2\text{-CF}_2)_n$ and its microstructure consists of polymer crystals within an amorphous matrix [58]. 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 has several advantages over the piezoelectric ceramic materials [32]. 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/cm^3).

It is noted that d_{33} value of PVDF polymer has the negative sign; that is, the film thickness decreases when an electric field 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 [59].

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 necessitating the use of amplifiers in close proximity to the transducer elements [56].

Other limitations of PVDF include its low electromechanical coupling factor ($k_t = \sim 0.2$), high required poling field and limited tolerance to the elevated temperatures [20,60]. 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 [53]. Since these copolymers contain a greater portion 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 ($< \sim 1$ MV/cm) can be used in these copolymers.

The piezoelectric properties of the copolymer have been measured for a wide composition range [53,61-64]. 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_{hg} 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 Matrix Phase : Thermoset Resin

2.4.1 Epoxy

Epoxy resins will retain their dominant position in the thermoset resin sector over the next 5 years despite competition from other resins that offer superior high-temperature performance. Although a number of factors serve to inhibit the development of radically new chemical systems, epoxy resin suppliers will continue to introduce innovations in response to the demand for improved processability and performance. Concerns regarding health and the costs involved in obtaining the necessary approval and registration of truly new chemical systems are major barriers to radical departures from established chemistry.

Starting materials for epoxy matrix are low-molecular-weight organic liquid resins containing a number of epoxide groups, which are three-membered rings consisting of one oxygen atom and two carbon atoms.



Figure 2.5 The epoxide group of epoxy matrix [65].

Epoxy matrix, as a class, has the following advantages over other thermoset matrices:

- a) A wide variety of properties because a large number of starting materials, curing agents, and modifiers are available
- b) An absence of volatile matters during cure
- c) Low shrinkage during cure
- d) Excellent resistance to chemicals and solvents
- e) Excellent adhesion to a wide variety of fillers, fibers, and other substrates
- f) High or low strength and flexibility
- g) Resistance to creep and fatigue
- h) Good electric properties
- i) Solid or liquid resins in the uncured state
- j) A wide range of curative options.

The principal disadvantages are its relatively high cost and long cure time, as well as

- a) Resins and curative somewhat toxic in uncured form
- b) Heat distortion point lowered by moisture absorption
- c) A change in dimensions and physical properties as a result of moisture absorption
- d) Use (dry) limited to about 200 °C upper temperature
- e) Difficult to combine toughness and high-temperature resistance
- f) A high thermal coefficient of expansion
- g) A high degree of smoke liberation in a fire
- h) May be sensitive to ultraviolet light degradation.

These resins cost more than polyesters and do not have the high-temperature capability of BMIs or PIs; but because of their advantages they are used widely.

The epoxy resins are capable of upper service temperatures in the range 125-175 °C, depending on the composition. The toughened versions of epoxy resins are tailored for use up to 125 °C, whereas the more rigid epoxy compositions are capable of service temperatures up to 175 °C.

The significant differences in the properties of the various epoxy materials are in the moduli, strains to failure, and glass transition temperatures. The glass transition temperature, which controls the use temperature of the various epoxy materials, is high (247 °C) for the brittle epoxies and much lower for the toughened epoxies (76 and 185 °C). Therefore, it is clear that one compromises the use of temperature to gain toughness in these resin materials. [65]

2.5. Piezoelectric Ceramic-Polymer Composites

It is instructive to compare the basic properties of the piezoelectric polymer, PVDF with those of 'PZT'. The flexibility and low density of the polymer contrasts with the stiffness, brittleness and high density of PZT. On the other hand the piezoelectric 'd' coefficient for PVDF is relatively small (~ -30 pC/N, the mechanisms by which the polarization in PVDF changes differ from those in PZT accounting for the different algebraic sign). However, because the relative permittivity of PVDF is low (~10) compared to that of PZT the voltage coefficients are similar in value.

Composite technology in general sets out to combine materials in such a way that the properties of the composite are the optimum for a particular determined by the choice of component and their relative amounts and, most importantly, the connectivity that is the manner in which the components are interconnected.

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 [66-99]. 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 [58]. More recently, the concept of composite material has been extended to other applications such as an ultrasonic transducer for acoustic imaging and sound absorbers. For these applications the transducer is usually interfacing with water or soft tissue, for example body skin. Furthermore, the advantages of piezoceramic-polymer include relatively good acoustic matching between transducer and medium, improved electromechanical coupling coefficient and higher band-width, the last allowing the engineering of well-defined ultrasonic pulses and in consequence good temporal and spatial resolution.

Sonar and imaging transducers transmit into and receive ultrasound energy from the surrounding medium and so are generating and experiencing hydrostatic pressure changes. The corresponding coefficients of significance are d_h and g_h , the former being a measure of the effectiveness of the transducer as a transmitter and the latter as a receiver. Because the transducer is required to be effective in both modes it is customary to introduce the product $d_h g_h$ as a 'figure of merit' (F.O.M) useful for comparing materials for this application. There are other critical considerations including the sharpness of the rise-time of the emitted pulse and the extent of the ringing following the pulse. Unacceptably long ringing would interfere with receiving a well-defined echo. The low mechanical Q of a polymer plays an important role in achieving good pulse characteristics.

The other important consideration concerns the transmission of ultrasound (and other forms of energy) from one medium to another and the importance of 'impedance matching'. When wave energy is transferred from one medium to another then a part is transmitted and the rest reflected. The ratio of reflected to transmitted energies depends on the characteristic impedances of the two media and the transmission is total if these are matched. In the case of acoustic waves the specific impedance (Z) of a medium is given by the product of the density ρ and the velocity of sound v that is $Z = \rho v$, Z is measured in 'rayl' (after Lord Rayleigh) and for water it has the value approximately 1.5 Mrayl ($\rho = 1000 \text{ kg.m}^{-3}$ and $v \sim 1500 \text{ m}^2.\text{s}^{-1}$); in the case of a typical PZT, Z is approximately 35 Mrayl and so the two are poorly matched. In contrast, for polymers Z is typically approximately 3.5 Mrayl and so the acoustic match with water is far better. A

further disadvantage of PZT is the high Q_m which is unsuited to the detection of sharp pulses because of the associated and troublesome ringing effects. [18].

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 [63]. The connectivity patterns and several types of piezocomposites will be described in the following subsections.

2.5.1 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.* [76,85] 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 2.6 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 2.7 represents the schematic diagram of different piezoelectric ceramic-polymer composites. All these composites showed improved piezoelectric properties compared to single phase piezoelectric ceramics.

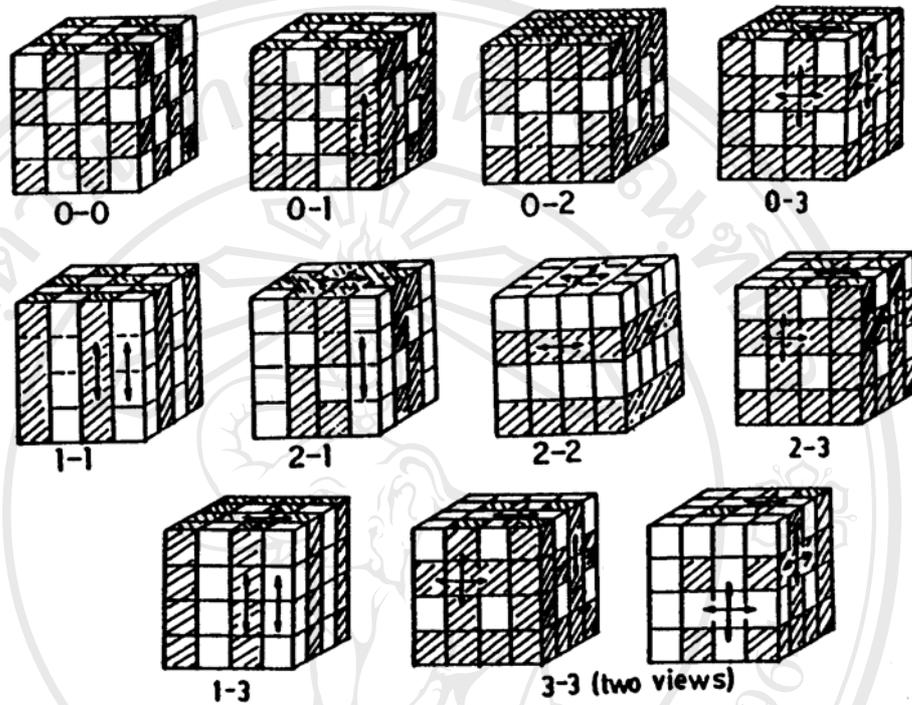


Figure 2.6 Ten different connectivity patterns of diphasic Materials [85].

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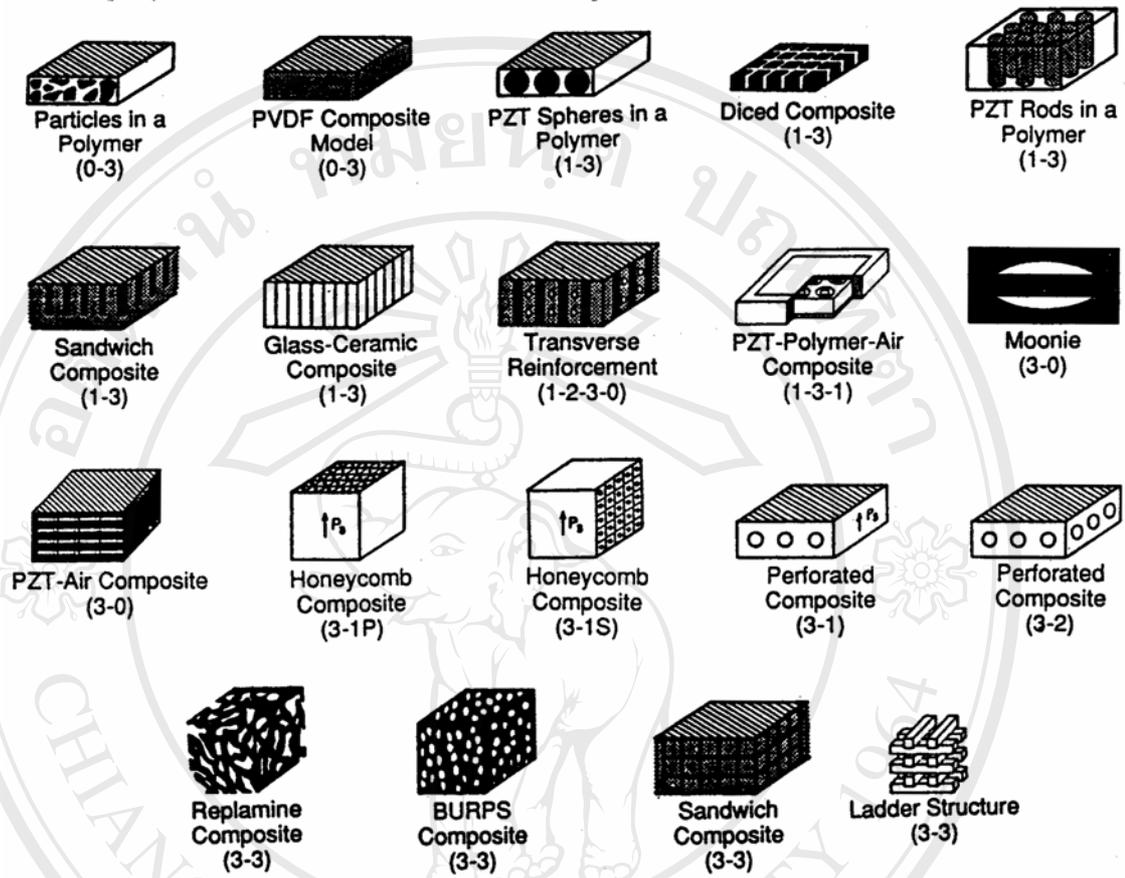


Figure 2.7 Schematic diagram of various piezoelectric ceramic-polymer composites

[85].

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2.5.2 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 2.8].

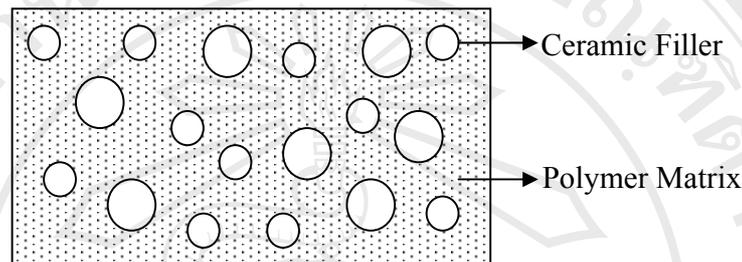


Figure 2.8 Schematic diagram of 0-3 ceramic-polymer composite.

In a composite with 0-3 connectivity, a three dimensionally connected polymer phase is loaded with ceramic powder. The major advantage of 0-3 is its ease of fabrication in a variety of forms including large flexible thin sheets, extruded bars and fibers, and molded shapes. It is also amenable to mass production and may conform to any curved surface. The properties of 0-3 composites are strongly dependent on the piezoelectric and polymer phases utilized, as well as the fabrication method employed.

Many different variations have been attempted, primarily for use in hydrophones and are summarized here.

The first attempts to produce 0-3 composites were made by Kyiatana [73], Pauer [74] and Harrison [75] using PZT as a filler material and polyurethane as a matrix. These early composites had very low d_{33} values.

Several types of flexible piezoelectric composites consisting of PbTiO_3 powder and chloroprene rubber were developed by Banno *et al.* [86-88] at NTG-NGK, namely PR-303, 304, 305, 306 and 307. PR-305 and 307 showed a figure of merit of $\sim 5000 \times 10^{-15} \text{ m}^2/\text{N}$, whereas PR-303, 304 and 306 showed a F.O.M. of $\sim 1000 \times 10^{-15} \text{ m}^2/\text{N}$. In addition, the F.O.M. of PR-305 and 307 showed signs of pressure dependence, whereas PR-303, 304 and 306 were pressure independent. In order to explain these variations, several piezoelectric composites consisting of PbTiO_3 powder with various particle sizes of 3.3, 7.3 and 31.8 μm were prepared. In addition, composites consisting of a binary PT ceramics powder with two distinct particle sizes of $A = 7.3 \mu\text{m}$ and $B = 31.8 \mu\text{m}$ were made. Several conditions were varied, including weight% solids loading. The properties were evaluated at pressures of 0.5 and 15 MPa, and the densities of the composites were measured by the Archimedes method. It was determined that both particle size and relative density affected d_h values. Larger sized particles seemed to produce higher d_h values, yet seemed to show moderate pressure dependence attributed to the porosity formation associated with the usage of larger particles. This was confirmed by relative density measurements, which was on the order of 93-96%. Smaller sized particles produced lower d_h values, but showed little or no pressure dependence, which was attributed to little or no porosity and was confirmed by relative densities approaching 100%. In considering the binary composites, the same effects listed above are applied.

The volume percent ceramic within the composite affected the d_h values. Composites with 40 volume% ceramic tended to show no pressure dependence. As the volume% of ceramic increased, the pressure dependence became more obvious and the

dh values decreased with increasing pressure. As with the large monosized particle composites, this too is due to porosity within the composites. More pores become trapped between the particles, causing dh to decrease with increasing pressure.

Giniewicz [100] developed 0-3 ceramic powder/polymer composites with a filler material of $0.5\text{PbTiO}_3\text{-}0.5\text{Bi}(\text{Fe}_{0.98}\text{Mn}_{0.02})\text{O}_3$ [PT-BF] composition. Composites prepared conventionally with water quenched PT-BF and Eccogel polymer exhibited a virtually pressure independent d_{hg} F.O.M. of $2700 \times 10^{10} \text{ m}^2/\text{N}$. Hanner *et al.* [101,102] developed a 0-3 paint composite containing polymer, piezoceramic powder (60-70 volume%) and the necessary surfactants and dispersants.

All of the piezoceramic filler materials mentioned were prepared by a mixed oxide method in which oxide raw materials are simply mixed together and calcined. Chemically derived piezoelectric powders offer the advantages of high purity, homogeneity of a molecular scale, lower processing temperatures and controlled particle size and distribution [103]. Flexible lead titanate/Eccogel 0-3 composites prepared with highly crystalline, coprecipitated ($\sim 3\mu\text{m}$) PT powder exhibited a much larger hydrostatic F.O.M. ($4170 \times 10^{10} \text{ m}^2/\text{N}$) than reported for mixed oxide PT composites [103,104].

Chemical processing was also used to prepared PT-BF (Mn doped) powder by the coprecipitation of an aqueous citrate-based solution [86]. Composites fabricatied by die pressing a mixture of the PT-BF powder and Eccogel polymer exhibited an excellent d_{hg} F.O.M. of $4200 \times 10^{10} \text{ m}^2/\text{N}$ [105].

Although the simplicity of 0-3 composite processing is highly desirable, it is difficult to achieve a completely uniform distribution of powder and polymer phases,

particularly at higher filler loadings. Furthermore, the presence of voids within the composites limits the poling field that may be applied by reducing the composite dielectric breakdown strength.

To improve the microstructural homogeneity and decrease the chance of void formation in 0-3 composites, a colloid processing method was developed by Han *et al.* at Rutgers University [106]. With this technique, piezoceramic powder was dispersed in a dilute polymer solution, allowing a polymer coating to be absorbed onto the powder surface. The addition of nonsolvent drives the polymer out of the solution and precipitates polymer-powder coacervates. Colloidal filtration, followed by die pressing, consolidated the coacervated, forming 0-3 composites with a uniform microstructure.

Colloidally processed composites composed of coprecipitated PT-BF powder and Eccogel polymer were measured to have the largest d_{33} (65 pC/N) and highest d_{hg} F.O.M. ($6000 \times 10^{10} \text{ m}^2/\text{N}$) of all true 0-3 composites. In addition, colloidally processed composites were able to withstand a poling field of up to 150 kV/cm as compared to 120 kV/cm for conventionally prepared composites with the same components. This is indicative of an improved composite microstructure resulting from the colloidal processing.

Han *et al.* studied the effect of the particle size on dielectric and piezoelectric properties of 0-3 composites [105]. In this study, composites of PT powder with different particle sizes and PVDF copolymer consisting of 90% vinylidene fluoride and 10% hexafluoropropylene were prepared. It was found that d_{33} decreased with the particle size of the filler material. It was also worthy noted that the d_{33} value decreased from 50 to 33

$\rho C/N$ as the particle size of the PT ceramic changed from 3.5 to 0.5 μm . Unlike the d_{33} behavior, the dielectric constant was found to be almost independent of the particle size of the ceramic filler except for slightly lower values in the composites with very fine particle sizes. The effect of the particle size on dielectric and piezoelectric properties were also investigated by Lee *et al.* [107]. In this work, PT powder of different particle sizes was mixed with Eccogel polymer and composites were prepared by conventional die pressing methods. They also observed that the dielectric constant and dissipation factor are not affected by particle size. However, d_{33} , decreased dramatically with particle size.

To investigate the effect of the polymer on resistivity and dielectric properties, Han *et al.* Prepared PT composites with Eccogel polymer, PVDF copolymer, and ethylene-propylenediene monomer (EPDM) polymer [105]. The PVDF copolymer and EPDM polymer had moderate resistivities (6×10^{14} and 10^{16} ohm.cm). It was found that although higher poling conditions could be applied to the PVDF copolymer and EPDM composites, the highest d_{33} value was obtained from the epoxy composites. The higher electrical conductivity of the polymer matrix may have created more electric flux paths between the ceramic particles. This in turn increased the electric field acting on the ceramic filler and made poling of the ceramic easier. The dielectric constant of the composite with EPDM polymer was slightly lower than that of the other two types of composites, but the dissipation factor of the composites with epoxy was two times larger than that of the PVDF copolymer and EPDM polymer. The epoxy gave the highest d_{hg} figure of merit (5600×10^{-15} m^2/N) and the EPDM gave the lowest figure of merit,

($600 \times 10^{-15} \text{ m}^2/\text{N}$). With the consideration of dissipation factor in the figure of merit, the PVDF copolymer gave the highest $d_{\text{hg}}/\tan\delta$ of $2000 \times 10^{-15} \text{ m}^2/\text{N}$.

One of the main problems in achieving 0-3 composites with high piezoelectric properties is the difficulty involved in poling the composites. In a 0-3 composite, the electric field which acts on an individual spherical piezoelectric grain is mostly controlled by the dielectric constant of the polymer phase. Since most polymers have a lower dielectric constant compared to piezoelectric ceramic materials, most of the applied electric field will pass through the lower dielectric constant phase. One way to resolve this difficulty with poling is to introduce a third conductive phase between the piezoelectric particles. Sa-Gong [108] prepared such composites by adding carbon, germanium or silicon to PZT. Another approach to ease the poling is to raise the resistivity of the ceramic filler material. This type of composite was prepared for PbTiO_3 powder doped with UO_2 to increase resistivity, allowing a very large (up to 130 kV/cm) poling field to be applied.

The poling of 0-3 composites can also be improved by using the corona poling method [109]. This technique in particular, has been successful in poling PVDF films.

In corona poling, charge is sprayed on the surface of an unelectroded sample creating an electric potential between the top sample surface and the ground plated. If the sample is defective the charge will leak through the film but the sample will not be entirely shortened because of the absence of electrodes. The set-up for the corona poling including one or more needles to which a large DC potential is applied. These needles act as field intensifiers by ionizing the surrounding gas molecules. The sample is

positioned on a heated and grounded metal plate. Heating makes poling easier by lowering the coercive field. The piezoelectric properties of ceramics and composites poled by the corona method are comparable or better than those poled by the conventional poling technique. Using this poling method, one can pole large area samples continuously.

2.5.3 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%) [66,110].

Recently, for the 1-3 type composites a minor impediment to evolution for large scale structures has been the problem of assembly. Recently Fiber Materials of Biddeford, Maine have applied their ultraloom technology originally evolved for thick section carbon/carbon composites to this problem. Using the ultraloom they are able to stitch PZT posts into a template structure which contains the transverse glass fiber reinforcement and make sections up to 4 feet in width and of almost any length.

The FMI composites are not only interesting for very large area hydrophones, but can also be used in an actuator mode. It is interesting to note that with only 5 vol% PZT and a resultant density of 2.2 gm/cm^3 the transverse coupling coefficient k_t at 0.70 is larger than that of solid PZT.

The 1-3 type concept has also been applied to transducers for medical ultrasonics (Shaulov, 1986, Gururaja *et al.*, 1984, Smith, 1986). Here the required frequencies are much higher $\sim 10 \text{ MHz}$ so that the scale is very much smaller and the rod structure can be cut from solid PZT. Beam characteristics, pulse shape and coupling factor are improved over solid PZT transducers.

Initially, 1-3 type piezocomposites were prepared using PZT rods that were extruded, sintered, and hot-pressed. 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 [79]. 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 [58]. 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_{hg_h} (20000×10^{-15} m²/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 [20]. They have low acoustic impedance (8.5 MRayls). And high g_{33} (100 mVm/N) as well as large ϵ (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 [110,111]. 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 [110].

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.* [80,81]. 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_{hh} ($3000 \times 10^{-15} \text{ m}^2/\text{N}$).

2.6 Piezoelectric Ceramic-Polymer 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 [34]. 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.

2.6.1 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 [34]. Thus, the piezoelectric materials for this application respond to the hydrostatic pressure, where all surfaces are stressed with equal amplitude. However, the details were described elsewhere [58,112].

Recently, an alternative hydrophone figure of merit was introduced taking into account the self-noise generated by the sensor material [113]. 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 $d_{hg}/\tan\delta$.

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 [20,114].

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 [58].

2.6.2 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 [20].

The dielectric constant is also important for the same reason it was for hydrophone applications. A $\epsilon_r \sim 100$ 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 [111].

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 [20]. 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 [110,111]. A $Q_m \sim 2-10$ is a compromise value that limits ringing within the transducer without external damping layers [20].

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 [110].

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 2.2.

Table 2.2 Optimum transducer material properties for low and high frequency applications [20].

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
ϵ_r	~100	~100
$\tan\delta$	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

2.7 Composite Processing and Fabrication

The fabrication of 0-3 composite is straightforward involving essentially the dispersal of piezoceramic particles in a polymer and forming the mixture into a shape by casting, moulding, extrusion, tape-casting, calendaring, etc. However, the variables are many and include composition of the ceramic particle, its shape and volume fraction; in the case of non-equiaxed particles then texture (the orientation of the particles with respect to the poling direction) is very significant and so too is the incorporation of porosity to tailor compliance in a controlled way.

In the case of 1-3 composites the variety of approaches to fabrication depends very much on the imagination and ingenuity of the fabrication technologist. For a comprehensive discussion is referred to the paper by V.E. Janas and A. Safari [115].

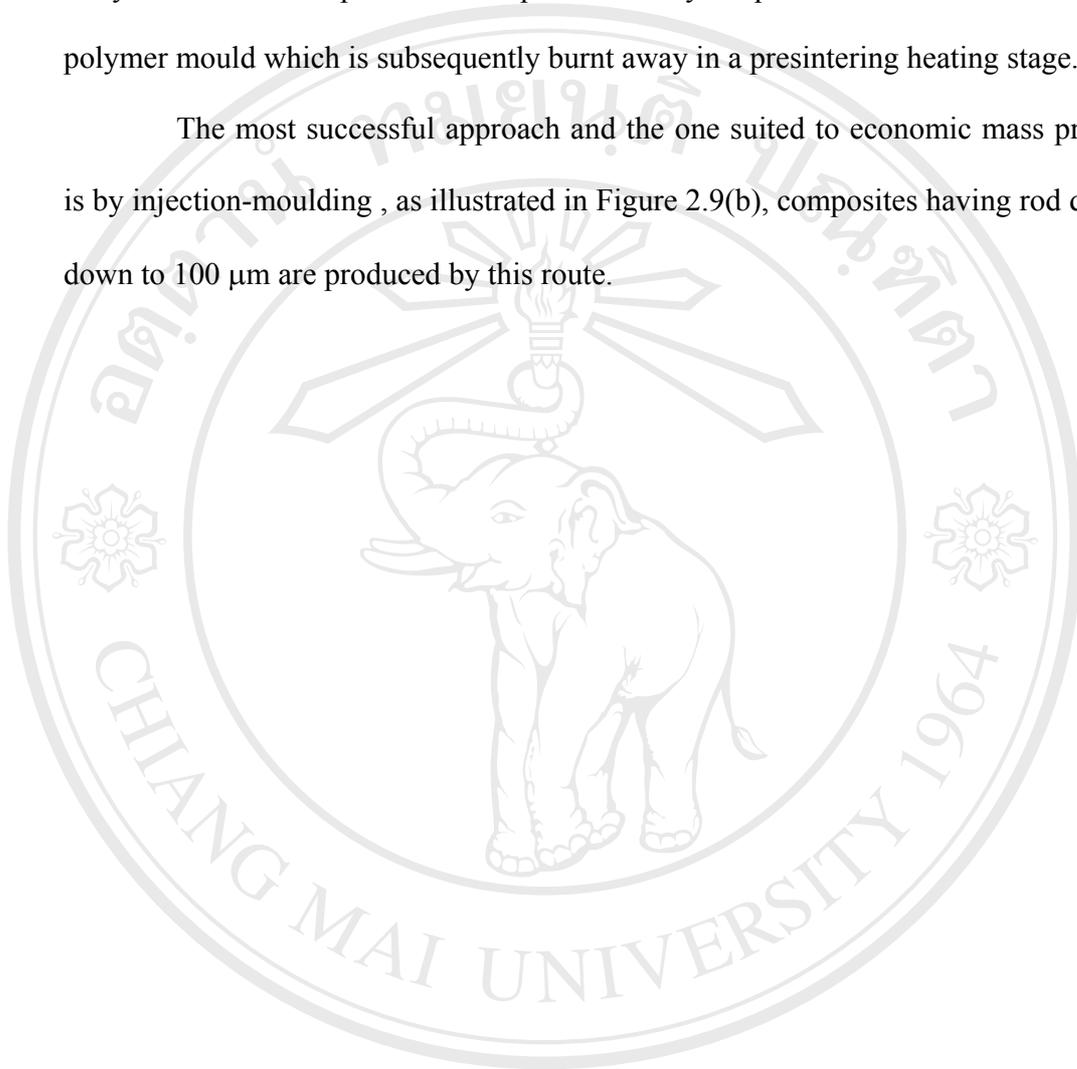
An obvious fabrication approach is the 'dice-and-fill'. A piezoceramic plate is diced into an array of square-section pillars standing on the undiced base of the plate. The structure is then in-filled with the chosen polymer after which the base is ground away to produce the structure shown in Figure 2.9(a). Typically rods of thickness sown to approximately 100 μm can be diamond-machined in this way.

In another approach extruded and sintered rods in reasonable lengths (~ 100 mm) are arranged in a jig, in-filled with the polymer the composite then being sliced into individual transducer plates. Again the lower limit on the rod diameter is approximately 100 μm .

Fine scale arrays ($< 50 \mu\text{m}$) have been produced by first making a metal master by hard X-ray lithography. This constitutes the mould from which a polymer 'negative'

array is made. The piezoceramic powder slurry or paste is formed in the 'sacrificial' polymer mould which is subsequently burnt away in a presintering heating stage.

The most successful approach and the one suited to economic mass production is by injection-moulding , as illustrated in Figure 2.9(b), composites having rod diameters down to 100 μm are produced by this route.



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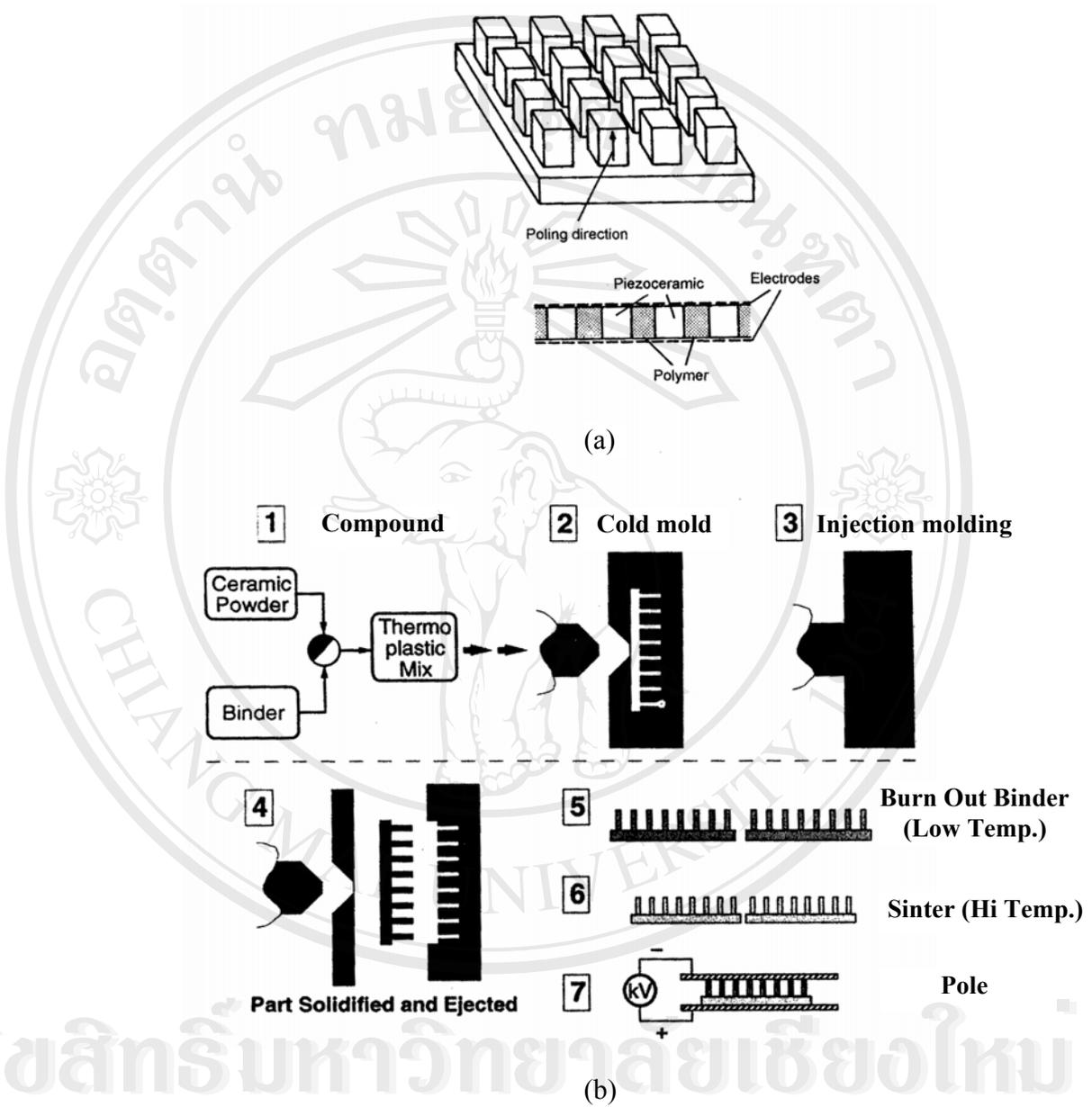


Figure 2.9 (a) 1-3 piezoceramic-polymer composite. (b) Fabrication the rod array for a 1-3 piezoceramic-polymer composite by injection moulding [18].

2.8. 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.