

## CHAPTER II

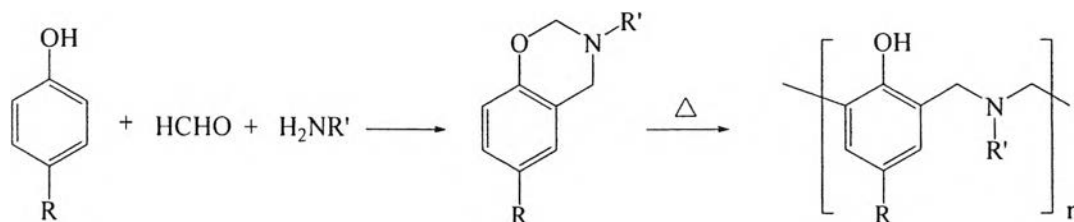
### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Polybenzoxazine

Traditional phenolic resins have been employed in a wide range of applications such as automotive and electrical industries because they have high chemical and heat resistance, dielectric insulators and also use inexpensive raw materials. However, the shortcomings of the traditional phenolic resins are the need for acid or alkaline as catalyst for polymerization, formation of void because of the water, a by-product during curing process, and large volumetric shrinkage upon curing. A series of polybenzoxazine obtained by the ring-opening polymerization of benzoxazine precursors has been developed as a novel type of thermosetting phenolic resin which overcomes several shortcomings of traditional phenolic resins, while retaining their benefit. Polybenzoxazine has excellent properties commonly found in the traditional phenolic resins such as heat resistance and flame retardance. It also provides properties that are not found in the traditional phenolic resin, such as excellent dimensional stability and low water absorption. In addition, the molecular structure of benzoxazine compounds were designed with great flexibility and it can be synthesized from inexpensive raw materials, cured without strong acid or alkaline, and does not release by-products during polymerization.

Benzoxazine monomers are synthesized via Manich condensation of derivative phenol, primary amine, and aldehyde. The benzoxazine monomer is a single benzene ring fused to another six-membered heterocycle containing one oxygen atom and a single nitrogen atom, called an oxazine ring. The oxazine ring is the reactive site for the curing of benzoxazine. A number of possible isomeric benzoxazines depend on the relative positions of the two heteroatoms and the degrees of oxidation of this oxazine ring system. Benzoxazine may be monofunctional or difunctional. The difunctional one can produce a crosslinked structure. The polymerization of the benzoxazine monomer is initiated by heat and obtained by ring opening polymerization (addition polymerization), as shown in Figure 2.1, so that there is no volatile by-product in the curing process. Various

combinations of amines and phenols have been used to synthesize benzoxazines. Polybenzoxazine has a repeating unit containing the form  $[-\text{Ph}(\text{OH})-\text{CH}_2-\text{NR}-\text{CH}_2-]$ . Molecular structures of the monomer and polymer contain a phenol and tertiary amine.



**Figure 2.1** Synthesis of benzoxazine monomers and polybenzoxazine (R=amine group, R'=phenol group).

Polybenzoxazine is a newly developed class of thermosetting resin that is based on the ring-opening polymerization of benzoxazine precursors, which were first synthesized by Holly and Cope (1944) through Manich reaction from phenols, formaldehyde, and amines. From the 1950's to the 1960's, Burke et al. synthesized many benzoxazines and naphthoxazines for the purpose of testing antitumor activity. The heated cured polymers from benzoxazine were firstly achieved by Schreiber (1973). Furthermore, Riess *et al.* (1985) studied the polymerization of mono-functional benzoxazines with and without phenolic as an initiator, resulting in linear polymers under 4000 molecular weight.

Ning and Ishida (1994) synthesized difunctional benzoxazine precursors. These polyfunctional benzoxazines were found to exhibit excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing. Furthermore, they offered greater flexibility than conventional phenolic resins in terms of molecular design. There are no strong acid or alkaline catalyst requirements and they do not release volatile by-products during the curing reaction.

Polybenzoxazine has unique properties that are not found in traditional phenolic resins. Ishida and Allen (1996) showed that the ring opening polymerization of polybenzoxazine occurs with either near-zero shrinkage or a slight expansion upon

curing. They exhibit excellent dimensional stability because of the ring opening mode of polymerization and have low rate of water absorption and low electric capacitance which are suitable for electrical applications.

Polybenzoxazine is expected to replace traditional phenolics, polyester, vinyl ester, epoxies, BMI, cyanate esters and polyimide in many respects. The molecular structure of polybenzoxazine offers superb design flexibility that allows properties of the cured material to be controlled for specific requirements of a wide variety of individual requirements. The physical and mechanical properties of the polybenzoxazine are shown in Table 1.1 to compare very favorably with those of conventional phenolic, epoxy resins, and performance polymer. The relative advantages of polybenzoxazine are obvious. They present a resin system with the highest tensile properties, and  $T_g$  can be boosted to as much as 340 °C through proper choice of the precursor phenol. This new family of phenolic resin features a wide range of mechanical and physical properties that can be tailored to various needs. From these properties, it indicates that polybenzoxazine is the resin for composite applications that possess high moduli and glass transition temperature, at low cross link densities. Impact, tensile, and flexural properties are also good. Results of the dielectric analysis on these polybenzoxazine demonstrate their suitability for electrical application (Nair, 2004).

Due to the excellent properties of polybenzoxazine, these make the polybenzoxazine suited for the matrix in composite applications. Previously, it was investigated as a polymer matrix in various composite materials to improve properties and also to reduce cost. Carbon fiber reinforced benzoxazine composite was studied by Shen and Ishida (1999A). The composite had low void content and gave high char yield, more than 87%. Good adhesion between fiber and matrix resulted in a balance between strength and toughness. The composite showed good mechanical properties, competing with polyimide composites and bismaleimide composites. Moreover, in the same year, a carbon fiber reinforced polynaphthoxazine composite was made through the same process and good results were also obtained (Shen and Ishida, 1999B). The boron nitride-filled polybenzoxazine was prepared for electronic packaging applications (Ishida and Rimdusit, 1998). This composite exhibited very high thermal conductivity because of highly thermally conductive

filler with a matrix resin which has low melt viscosity and good adhesion to the filler. The molding compound also exhibited high and stable mechanical strength up to 200 °C with a high  $T_g$  value of 220 °C. Water absorption at room temperature for 24 h of this composite is very low. A polybenzoxazine-montmorillonite hybrid nanocomposite was successfully prepared by Agag and Takeichi (2000). These nanocomposites have higher thermal stability than pristine polybenzoxazine. The storage moduli and the char yield increased with increasing the montmorillonite (OMMT) content.

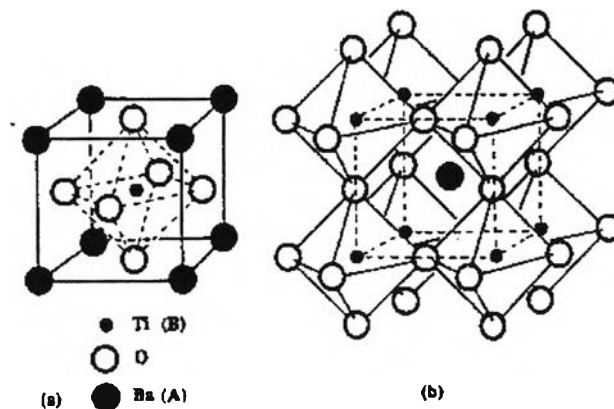
**Table 2.1** Comparative properties of various high performance polymers (Nair, 2004)

Properties	Epoxy	Phenolic	Bisox-phen (40:60)	P-T resin	PBZZ
Density (g/cm <sup>3</sup> )	1.2-1.25	1.24-1.32	1.3	1.25	1.19
Max use temperature (°C)	180	200	250	300-350	130-280
Tensile strength (MPa)	90-120	24-45	91	42	100-125
Tensile modulus (GPa)	3.1-3.8	03/05	4.6-5.1	4.1	3.8-4.5
Elongation (%)	3-4.3	0.3	1.8	2	2.3-2.9
Dielectric constant (1 MHz)	3.8-4.5	04/10	-	3.1	3-3.5
Cure temperature (°C)	RT-180	150-190	178-225	177-316	160-220
Cure shrinkage (%)	>3	0.002	<1	~3	~0
TGA onset (°C)	260-340	300-360	370-390	410-450	380-400
$T_g$ (°C)	150-220	170	160-295	300-400	170-340
G IC ( J/m <sup>2</sup> )	54-100	-	157-223	-	168
K IC (MPa m <sup>1/2</sup> )	0.6	-	-	-	0/94

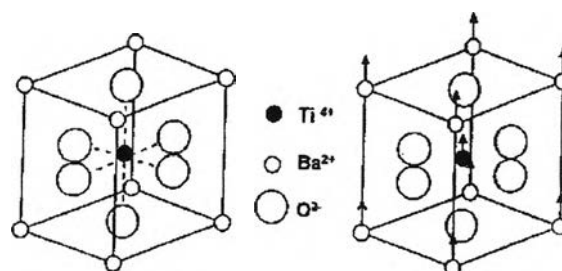
## 2.2 Barium Titanate and Barium Strontium Titanate

### 2.2.1 Perovskite Crystal Structure

Pure crystalline  $\text{BaTiO}_3$  has the perovskite structure, as shown in Figure 2.2. This structure has cubic unit cell consisting of bivalent barium ions ( $\text{Ba}^{2+}$ ) at the corner, a small tetravalent titanium ions ( $\text{Ti}^{4+}$ ) at the center, and bivalent oxygen ions ( $\text{O}^{2-}$ ) at the face center. The barium ions are surrounded by twelve nearest-neighbors oxygen ions. The titanium ions are surrounded by six oxygen ions located at the corners of an octahedron. The barium ions and oxygen ions together form a cubic closely packed array with titanium ions fitting into octahedron interstices (Buchanan, 2004).



**Figure 2.2** (a) A cubic  $\text{ABO}_3$  ( $\text{BaTiO}_3$ ) perovskite-type unit cell and (b) three dimension network of corner sharing octahedral of  $\text{O}^{2-}$  ions.



**Figure 2.3** The crystal structure of  $\text{BaTiO}_3$ : (a) above the Curie point the cell is cubic and (b) below the Curie point, the structure is tetragonal with  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  ion displaced relative to  $\text{O}^{2-}$  ions.

### 2.2.2 Ferroelectricity in Barium Titanate

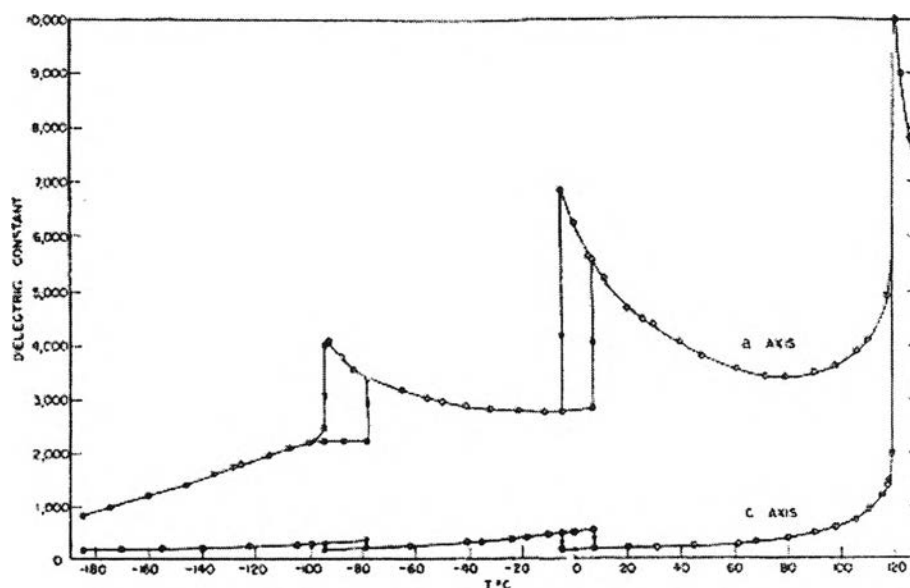
The paraelectric cubic phase of the pure BaTiO<sub>3</sub> is stable only above 130 °C, which is defined as the Curie temperature. The Curie point is the temperature where is a phase changing from paraelectric phase to tetragonal phase. Below Curie temperature, the titanium ions become displaced from the central position in the TiO<sub>6</sub> octahedra of unit cell, shown in Figure 2.3. The displacement of titanium ions creates a non-uniform distribution of electric charge leading to the formation of electric dipoles and spontaneous polarization in the unit cell. BaTiO<sub>3</sub> ceramics are ferroelectric because the direction of this spontaneous polarization can be responded by an electric field. Below Curie temperature, there are three ferroelectric forms:

1) A tetragonal distortion of the BaTiO<sub>3</sub> structure exists between 130 and 0 °C, with the spontaneous polarization aligned along the original [100] direction of the perovkite unit.

2) An orthorhombic distortion of the BaTiO<sub>3</sub> structure exists between 0 and -90 °C, with the spontaneous polarization aligned along the original [110] direction of the perovkite unit.

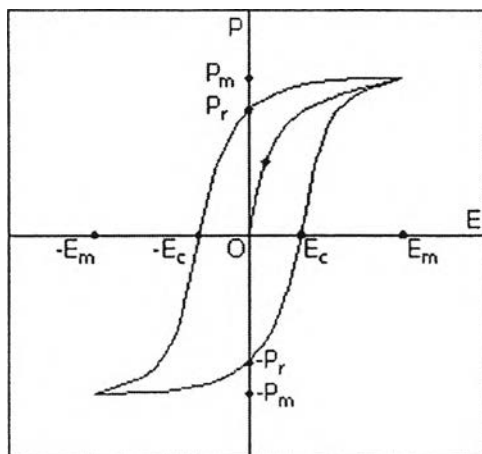
3) A rhombohedral (trigonal) distortion of the BaTiO<sub>3</sub> structure exists below -90 °C, with the spontaneous polarization aligned along the original [111] direction of the perovkite unit.

The temperature at which the crystal transforms from one ferroelectric phase to another is called transition temperature (Swartz, 1990). The variation of dielectric constant as function of temperature for BaTiO<sub>3</sub> is show in Figure 2.4. Near Curie point or transition temperatures, thermodynamic properties, including dielectric, elastic, optical, and thermal constant, show anomalous behavior. This is due to a distortion in the crystal as the phase structure changes (Merz, 1949).



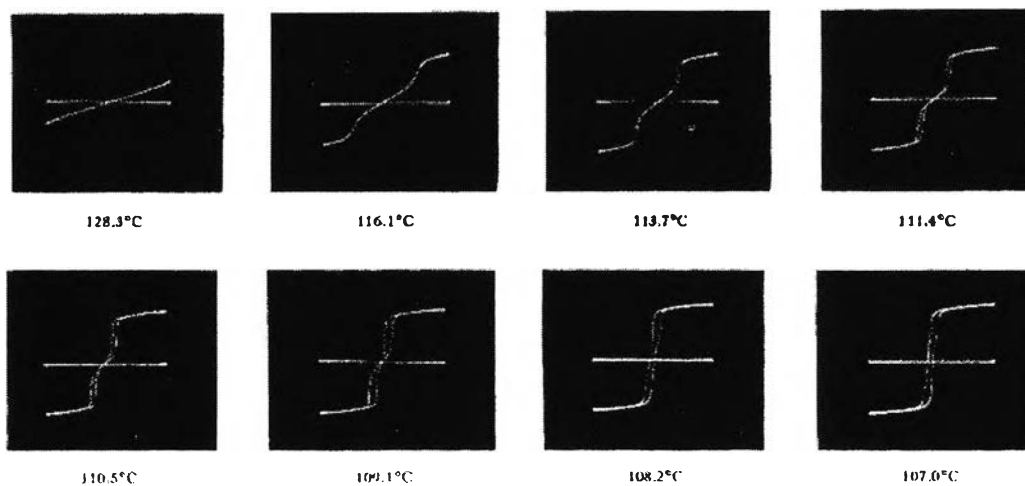
**Figure 2.4** Variation of dielectric constant as function of temperature for BaTiO<sub>3</sub>.

As mentioned above, the most important characteristic of ferroelectric materials is polarization reversal (or switching) by an applied electric field. This polarization reversal process is observed by measurement of ferroelectric hysteresis. The relation between polarization ( $P_r$ ) and applied electric field ( $E$ ) measured by the method of Sawyer and Tower shows hysteresis loop, as shown in Figure 2.5. At small values of the applied electric field, the polarization increases linearly with the field amplitude. In this region, the field is not strong enough to switch domains with the unfavourable direction of polarization. As the field is increased the polarization of domains with an unfavourable direction of polarization will start to switch in the direction of the field. At high field, the polarization reaches a saturation value ( $P_{sat}$ ). When the direction of the field is reversed, the polarization is switched to the opposite orientation and the measured polarization has the opposite sign. The remanent polarization ( $P_r$ ) corresponds to the polarization at zero field. There are two polarization values at zero field, corresponding to the two different orientation. The coercive field ( $E_c$ ) is the magnitude of electric field required to switch the orientation of the polarization. Ideally, hysteresis loop is symmetry so that  $+E_c = -E_c$  and  $P_{sat} = P_r$  (Damjanovic, 1998).



**Figure 2.5** Ferroelectric ( $P$ - $E$ ) hysteresis loop.

The electrical polarization  $P$  versus applied field  $E$  curve of  $\text{BaTiO}_3$  was observed by Merz (1953). The experimental data have been obtained from a series of hysteresis loops shown in Figure 2.6 at different temperatures. At higher temperatures, it shows a linear relationship which indicates the paraelectric cubic phase. At lower temperature, they showed a hysteresis loop which refers to the ferroelectric phase.



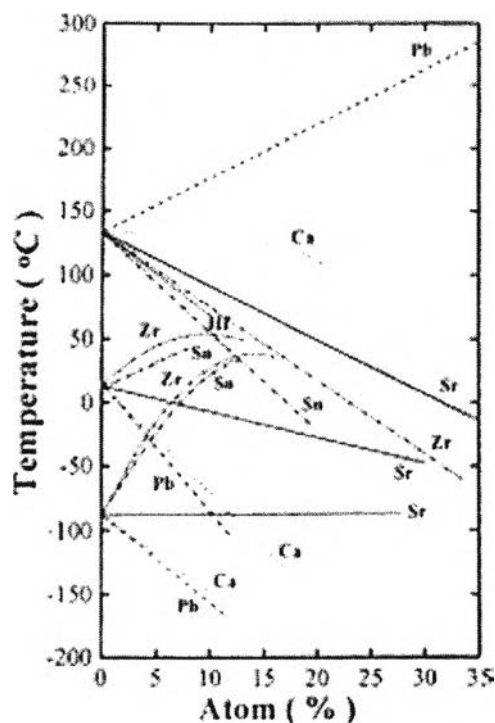
**Figure 2.6**  $P$ - $E$  curve of  $\text{BaTiO}_3$  at different temperature.



### 2.2.3 Ceramic Powder Preparation

Conventionally,  $\text{BaTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  powders are prepared by solid state reaction. The starting materials typically include carbonate ( $\text{BaCO}_3$  and  $\text{SrCO}_3$ ) and titanium oxide ( $\text{TiO}_2$ ). However, ceramic powders obtained from the solid state reaction have some drawbacks such as large particle size with uncontrolled and irregular morphology and higher impurity due to repetitive calcinations and grinding treatments and also lower chemical reaction (Deshpande *et al.*, 2005). These drawbacks can limit the dielectric properties of the resulting sintered ceramics. In order to obtain desired properties of  $\text{BaTiO}_3$  powders, various chemical methods have been recently proposed for preparing high purity and fine powder. These methods involve hydrothermal synthesis, oxalate precipitation, sol-gel process or thermal decomposition of metal alkoxide, etc (Kareiva *et al.*, 1999). Among these methods, the sol-gel method was used because of particular advantages in obtaining fine ceramic powders with high chemical purity, narrow size distribution, and homogeneity through a lower temperature process, avoiding contamination of the materials. Also, it helps to maintain homogeneous mixing of two cations at molecular level (Yang *et al.*, 2002).

Hu *et al.* (2004) could prepare the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  powders by sol-gel process calcined at 800 °C for 2h with the particle sizes of 50-100 nm, which are smaller than powder prepared from conventional solid state reaction. Also, their sintering temperature is lower (1250 °C). Deshpande *et al.* (2005) synthesized sol-gel  $\text{BaTiO}_3$  powder by calcined at 750 °C for 6 h, producing powder with submicron size and spherical shape. Tangwiwat and Milne (2005) reported that sol-gel  $\text{BaTiO}_3$  powder appeared perovskite structure after calcinations at 600 °C, but intermediate barium carbonate phase were also observe. Therefore, calcination at 1000 °C was required to obtain single phase  $\text{BaTiO}_3$  powder.



**Figure 2.7** The effect of isovalent substitutions on the transition temperatures of  $\text{BaTiO}_3$ .

Previously, the addition of various isovalents (e.g.  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ , etc.) into  $\text{Ba}^{2+}$  has been studied with the aim of obtaining improved dielectric properties. In this study, we have focused on the addition of strontium, which is usually employed to shift Curie point toward to room temperature for particular application and to maintain a fairly low temperature dependence of the dielectric constant. The  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  can be obtained by substitution of isovalent additive  $\text{Sr}^{2+}$  replacing  $\text{Ba}^{2+}$  in perovskite structure. The  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  is ferroelectric at room temperature for barium rich composition ( $x < 0.35$ ) (Fu *et al.*, 2005). Increasing the strontium content allows the Curie point shifted below room temperature. In this way,  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  can be made paraelectric at room temperature. The effect of various isovalent substitutions on the transition of ( $\text{BaTiO}_3$ ) ceramic are shown in Figure 2.7.

#### 2.2.4 Dielectric Properties

The dielectric properties of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  are sensitive to microstructure (grain size). The calcining temperature is important because it influences the density and dielectric properties of the final product. The higher the calcining temperature, the higher the homogeneity and density of the final ceramic product. The calcined powder should be completely single phase. Incomplete calcination results in enhanced sintering and abnormal grain growth. However, prolonged calcination time increases the particle size and decreases the sintered density of the ceramic. So, proper calcination at a certain temperature is necessary to obtain the best electrical and mechanical properties Su *et al.* (2002). Moreover, the sintering temperature and time should be optimum for proper densification to occur without abnormal grain growth. The sintering of oxide ceramic must be carried out in an oxidizing atmosphere or in air. Zhang *et al.* (2005) found that the grain size and dielectric constant of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  increase with increasing sintering temperature. Abdelkefi *et al.* (2005) reported that prolonging sintering time is also effective to increase the grain size and improve the microstructure homogeneity.

The best known example of the effect of microstructure on the properties of the ceramic is the grain-size dependence on the dielectric properties. The variation of dielectric constant with temperature of  $\text{BaTiO}_3$  ceramics was found to be dependent on the grain size with a fine ( $\sim 1 \mu\text{m}$ ) and coarse ( $\sim 50 \mu\text{m}$ ) grain size. The large grain of the  $\text{BaTiO}_3$  shows an extremely high dielectric constant at the Curie temperature. This is due to the formation of multiple domains in a single grain, the motion of domain walls provide large contribution to the dielectric constant at the Curie temperature. For  $\text{BaTiO}_3$  ceramics with fine grains ( $\sim 1 \mu\text{m}$ ), a single domain forms inside each grain. The domain walls are restricted by the grain boundaries resulting in difficult to move. The absence of domain wall motion in fine grained ceramics results in lower dielectric constant at Curie temperature. The effect of grain size on the dielectric constant at room temperature was explained by Arlt *et al.* (1985). They proposed that the internal stresses in fine grained  $\text{BaTiO}_3$  must be greater than the coarse grained ceramic because ferroelectric deformation becomes more difficult to release, thus leading to higher dielectric constant at room temperature. However, the dielectric constant is low as decreasing grain size to sub-

micron range, because the stresses make smaller contribution to the dielectric constant.

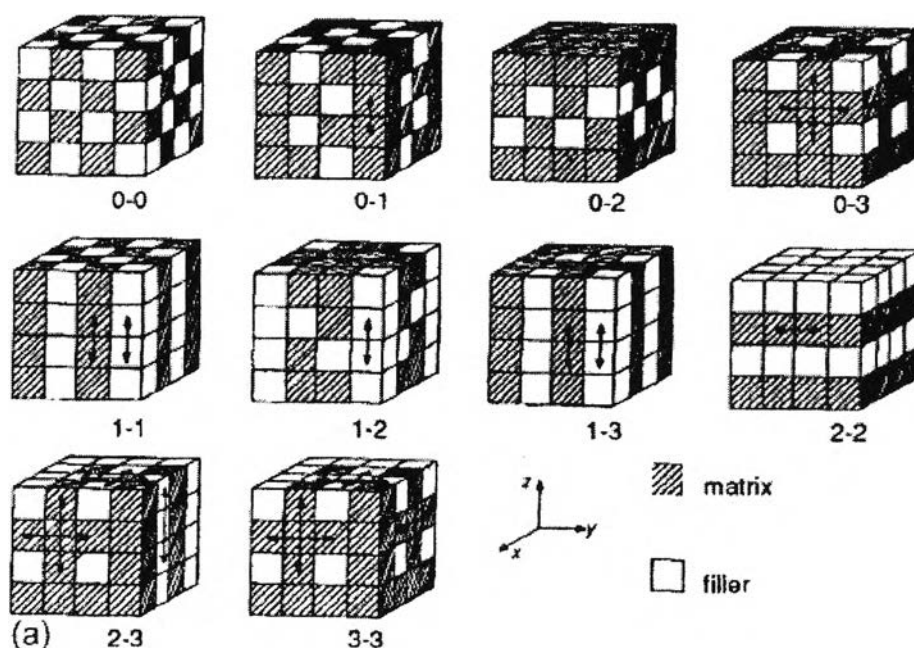
Moreover, the dielectric properties were also measured as function of frequency and electric field. Wu *et al.* (2000) reported the drop of dielectric constant and abruptly increase of dielectric loss at high frequency, which are due to dipolar relaxation in the ceramic. In order to improve dielectric properties at microwave frequency, the dopant (MgO) have been used to suppress dielectric loss of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  for microwave application (Lin *et al.*, 2005). Previously, many literatures have been studied the dielectric properties of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ceramics in ferroelectric phase. However, few studies have been reported the dielectric properties in the paraelectric state. The dielectric loss, which is important factor in electronic application, is usually lower in paraelectric state than in the ferroelectric state (Liou and Chiou, 1998). Therefore, the  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ceramic in both paraelectric and ferroelectric were observed in this study.

### 2.3 Polymer-Ceramic Composite

Composite material by the combination of ceramic and a polymer combines superior properties of both polymer and ceramics, which results in far better performance than those of the constituent materials. The ceramics possess high dielectric constant but poor mechanical properties (brittleness), low dielectric breakdown strength and require a high temperature process. On the other hand, polymers are flexible, easy to process at low temperature, and possess a high dielectric breakdown field. By the combination of these two, composite materials with high dielectric constant, good mechanical strength, ease of processing and high breakdown field to achieve high volume efficiency and energy storage density for application of capacitor, electric energy storage devices and transducer can be developed. The design of composites with optimum properties becomes very challenging since the electro-active properties not only depend on the materials and the compositions, but also on their interconnections (Bai *et al.*, 2000).

Making a ceramic-polymer composite means not only choosing the right materials processed in a particular way but also coupling them with the best possible

design structure. In 1978, Newnham et al. developed the concept of connectivity to describe the arrangement of the component phase in composites. In a composite, each phase is spatially self-connected in either one, two or three dimensions. In a diphasic or two phase system, there are ten different combinations of phase connectivity which are indicated using two digits, denoting the connectivity of the filler and that of the matrix in that order. These are the 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, and 3-3 connectivities represented in Figure 2.8 using a cube as a building block. The types of connectivity are shown in the form A-B where A refers to the number of direction in which the active phase (ceramic) is self connected or continuous. B shows the continuity directions of the passive phase (polymer) (Safari, 1994). Among the composites studied so far, the most commonly composites is the 0-3 connectivity because of its ease of fabrication in a variety of forms including flexible thin sheets, extruded bars and fibers, and certain molded shapes. This type of composite is also amenable to mass production at a relatively low cost.



**Figure 2.8** Connectivity patterns in a diphasic composite system.

For making composites of ceramic and polymer, the dielectric constant of the composites is an important parameter for application. The dielectric constant

should be as high as possible. On the other hand, the loss tangent should be as low as possible. Therefore, the dielectric behavior of composites was investigated in many works. The results show that dielectric behaviors are strongly influenced by the ceramic phase (content, particle size and distribution) and processing techniques are very important because dielectric performance of the final composite can be affected by porosity or filler distribution. The dielectric constant of composites increases with increasing amounts of ceramic. The necessary amount of ceramic filler has to be enough (more than 30% in volume) to change the dielectric constant of the composite, but these high levels may make processing the materials more difficult.

There are many types of polymer used for mixing with ceramic to obtain 0-3 composites. Thermosetting polymer (epoxy and polyimide) are generally used for electronic application, especially embedded capacitor application because of its compatibility with print circuited wiring board (PWB) and good thermal stability (Kuo *et al.*, 2001). The first attempts to produce 0-3 composites were made by Kiyatama, Pauer, and Harrison using PZT as a filler material and polyurethane as the matrix. These early composites had very low  $d_{33}$  value. In this section, reviews cover ceramic/polymer composites which have  $\text{BaTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  as ceramic fillers because they are the ceramics that are used in this research work.

The effects of the ceramic particle size on the dielectric a properties of the ceramic-polymer composites were investigated in previous study. Lee and Kim (1989) fabricated the composites of  $\text{BaTiO}_3$  and phenolic resin. These composites were investigated for their dielectric properties with the ceramic particle size in the range of 2 to 130  $\mu\text{m}$ . Under the condition of the same density and ceramic/polymer volume ratio of the composite, the dielectric constant of the composite increase as the particle size of  $\text{BaTiO}_3$  in the composite increases. For the dielectric constant versus temperature of various particle size of  $\text{BaTiO}_3$  in the composite, the dielectric constant is smaller and the dielectric is broadened with decreasing particle size. Hsiang *et al.* (2001) studied the effect of particle size of  $\text{BaTiO}_3$  powder on the dielectric properties of  $\text{BaTiO}_3/\text{PVDF}$  composites. They found that the dielectric constant and loss tangent for composites increased with increasing  $\text{BaTiO}_3$  particle size when the frequency was above 100 kHz. On the other hand, the opposite results were obtained for frequencies below 100 kHz.

Popielarz *et al.* (2001) studied the effect of different polymer matrices on the dielectric properties of the composites. It has been found that for the same BaTiO<sub>3</sub> content, the dielectric constant of the composite strongly depends on the type of polymer. Polar polymers increase dielectric constant of the composite at low frequencies but have little effect at gigahertz frequencies. However, the presence of polar groups in the polymer matrix also increases loss tangent, particularly within the intermediate frequency within the megahertz to gigahertz range.

Kuo *et al.* (2004) reported the self-synthesized BaTiO<sub>3</sub>/epoxy composites had the best dielectric property. Its 40% filler composite had a dielectric constant of 44, which was higher than that of 27 for commercial BaTiO<sub>3</sub> composites. The large ceramic aggregates formed in epoxy matrix are the reason for the self-synthesized BaTiO<sub>3</sub>/epoxy composite having a higher dielectric constant of 44. The composite dielectric constants remain constant with test temperature and frequency. The composite with a low porosity lead to a low loss tangent.

Cheng *et al.* (2006) studied the dielectric constant of the epoxy containing 80 wt% (45 vol%) of BaTiO<sub>3</sub> in microwave frequency. It was found that the dielectric constant could be increased from 3.2 to 13.1.

Liou and Chiou (1998) investigated the dielectric characteristic as a function of temperature in the range of 0 to 100 °C of barium strontium titanate (BST)/silicone-rubber composite. The BST powders have particle sizes of 5-10 μm. The dielectric constant decreases with increasing temperature. A broadening of dielectric peak was observed. Moreover, the variation of dielectric constant with frequency becomes less as the volume fraction of BST decreases. The dielectric constant for 64% BST rapidly declines above 1 MHz.

Cho *et al.* (2002) reported that a dielectric constant value of 93 showed up at higher volume loading, 80 vol% and also that there was a sudden drop past 80 vol%. This drop in the dielectric constant can be attributed to the excessive porosity in the composite, which has a deleterious effect on the dielectric constant. Defects such as voids and porosity tend to decrease the dielectric constant due to the fact that pores behave as a matrix of air (dielectric constant of 1). However, this problem was solved by Davaraju *et al.* (2005). They could achieve in increasing the dielectric constant above 80 vol% of BaTiO<sub>3</sub> by treating BaTiO<sub>3</sub> with surfactant BYK-W9010,

which help to good dispersion without agglomeration. Polyimide/BaTiO<sub>3</sub> composites have stable dielectric constants in the frequency range of 1 kHz – 1 MHz with various ceramic contents. A dielectric constant as high as 125 has been attained at a frequency of 1 kHz (117 at 1 MHz) for a ceramic content of 90 vol%. The loss tangent increases with an increasing of ceramic in the composite content because of the increasing porosity in the composites.

Loss tangent of a material, which limits the frequency selectivity, is influenced significantly by extrinsic factors such as porosity, microstructure, and defects. The BaTiO<sub>3</sub> containing bulk samples had higher loss tangent, as compared to their thick films. The difference is caused by the porosity produced by different processes. The porosity of BaTiO<sub>3</sub> containing bulk composites decreases with ceramic ratio up to 30%, then increases abruptly at 40%. The higher porosity for the 40% BaTiO<sub>3</sub>/epoxy bulk composites leads to higher loss tangent (Kuo *et al.*, 2004).

Previously, many methods have been proposed to improve the microstructure homogeneity and decrease the chance of void formation in 0-3 composites in order to create uniformity of the properties and higher dielectric constant. Rao *et al.* (2003) found that surface treatment of the ceramic using di-block copolymer surfactant help to achieve the high dielectric constant of the composites at low ceramic loading by improving ceramic dispersion, which is better than monomer surfactant. Li *et al.* (2004) reported the phthalocyanine-coat BaTiO<sub>3</sub> was prepared to increase the dielectric constant of nanocomposite. Its dielectric constant was measured to over 80 at 1 MHz, which was much higher than that of composite derived from commercial BaTiO<sub>3</sub>. Xie *et al.* (2005) successfully synthesized BaTiO<sub>3</sub>/polyimide composites through a colloidal process by blending the coupling agent modified BaTiO<sub>3</sub> particles into a polyimide solution. The composite incorporating 50 vol% BaTiO<sub>3</sub> has the dielectric constant and loss tangent of 35 and 0.0082, respectively, at 10 kHz. The dielectric properties of the composites displayed good stability within a wide range of temperature or frequency. Also, thermal stability could be improved with the incorporation of BaTiO<sub>3</sub>.

To explain and predict the effect of each phase on the dielectric properties of the composites, several quantitative rules of mixture models have been proposed for the prediction of the dielectric constant of 0-3 ceramic/polymer composites.



However, while different models have been developed, little or no experimental evidence has been provided to support the derived equations, and the most theoretical models fail when they come to prediction of the dielectric constant of the ceramic/polymer composites, where there are large contrasts between the dielectric constants of the components, especially at high ceramic contents. The dielectric properties of composites depend on four factors; the properties of the constituent phase, their intervening volume fraction, and the way in which they are connected. The fourth factor of emulating the microgeometry of the inclusions can also be of considerable importance in 0-3 composites (Dias and Das-Gupta, 1996). In this study, various dielectric mixing models including the Yamada model, the Litchnecker model, the Bruggemann formulae, the modified Kerner expression will be fitted with the experimental results in order to select the model that can fit well with experimental results and confirm the 0-3 connectivity of ceramic filler in composite type.

## 2.4 Dielectric in Solid Materials

Dielectric properties comprise the non long-range conducting electrical characteristic of a material. Dielectric responses result from the short-range motion of charge carrier under the influence of an applied electric field. The motion of the charges leads to the storage of electrical energy and the capacitance of the dielectric. Consequently, as a first step in examining dielectric behavior, let us consider the definition of *capacitance*. Capacitance is a measure of the ability of any two conductors in proximity to store a charge  $Q$ , when a potential difference  $V$  is applied across them.

$$C = \frac{Q}{V} = \frac{\text{Coulombs}(C)}{\text{Volt}(V)} = \text{Farad}(F) \quad (2.1)$$

The capacitance of a vacuum capacitor is determined purely by the geometry. It can be shown from elementary electro-statics that the charge density on the plates,  $Q$  is proportional to the area  $A$  in square meters and the electric intensity applied  $E = V/d$ , where  $d$  is the distance between the plate (in meters). The proportionality constant is defined as  $\epsilon_0$ , the permittivity of free space, and is equal to

$8.854 \times 10^{-12} \text{ C}^2/\text{m}^2$  or F/m. Thus, the capacitance of a parallel-plate capacitor will be equal to:

$$Q = qA = \pm \epsilon_0 EA = \epsilon_0 (V/d)A \quad (2.2)$$

$$C_0 = Q/V = \frac{\epsilon_0 (V/d)A}{V} = \epsilon_0 A/d \quad (2.3)$$

When a material is inserted between the plates the capacitance is increased. The relative dielectric constant of the material  $k'$  is defined as the ratio of the capacitance of a condenser, or capacitor, with a dielectric between the plates to that with a vacuum between the plates.

$$k' = \frac{C}{C_0} = \frac{\epsilon' A/d}{\epsilon_0 A/d} = \frac{\epsilon'}{\epsilon_0} \quad (2.4)$$

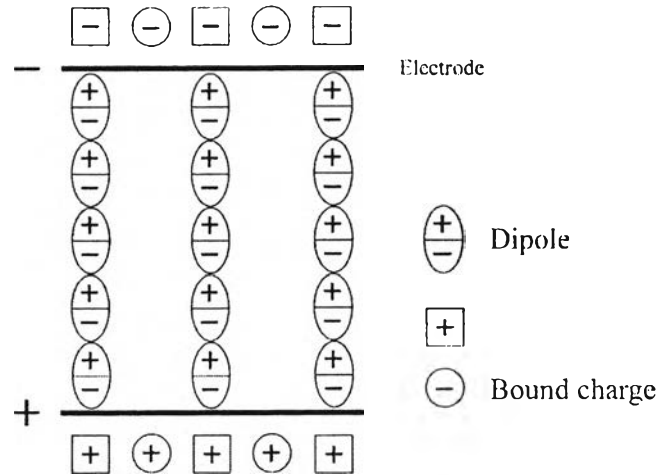
where  $\epsilon'$  is the permittivity of the dielectric material, also in unit of  $\text{C}^2/\text{m}^2$  or F/m.

Thus the dielectric constant of a material is the ratio of the permittivity of the material to the permittivity of free space. Consequently, the dielectric constant  $k'$  is also called the relative permittivity in some literature.

A dielectric material react to an electric field differently from a free space because it contain charge carriers that can be displayed, and charge displacements within the dielectric can neutralize a part of the applied field . Some charges can drift through the material to be discharged at the electrodes, while other charges are bound and can only oscillate to produce a polarization. The total electric displacement field  $D$  in the material is a measure of the sum of current flow from the shifting charge and can be related to the electric field through the permittivity of material by

$$D = \epsilon_0 E + P = \epsilon' E \quad (2.5)$$

where  $P$  is the resultant polarization or surface charge density of the material caused by the bound charge. Figure 2.9 represents the dielectric polarization by dipole chain and bound charges of the dielectric material.



**Figure 2.9** Schematic representation of dielectric polarization.

The polarization  $P$  is equal to the total dipole moment induced in the material by the electric field. Thus

$$P = \sum_i N_i \mu_i \quad (2.6)$$

where  $N$  is the number of dipole per unit volume and  $\mu$  is the dipole moment relating two opposite charge ( $q$ ) separated by a distance  $d$  by  $\mu = qd$ . Thus polarization can equivalent designate either the bound-charge density or the dipole moment per unit volume. From equation (2.6)

$$P = E(\epsilon_0 k^* - \epsilon_0) = \epsilon_0 (k^* - 1)E \quad (2.7)$$

And rearranging:

$$k^* - 1 = \frac{P}{\epsilon_0 E} \quad (2.8)$$

And defining:

$$\frac{P}{\epsilon_0 E} \equiv \chi, \text{ the electric susceptibility} \quad (2.9)$$

The susceptibility is the ratio of the bound charge density to the free charge density.

The dielectric loss relate to the polarization and current in an alternating field. The time required for polarization is reflected as a phase retardation of the charging current. Instead of being  $90^\circ$  advanced of the voltage, the current is advanced by some angle  $90 - \delta$ , with difference generally referred to as the loss angle

( $\delta$ ). Representing the electric field and the displacement (flux density) in complex notation:

$$E = E_0 e^{i\omega t} \quad (2.10)$$

$$D = D_0 e^{i\omega t} \quad (2.11)$$

And making use of the relation

$$D = k^* E \quad (2.12)$$

One obtains

$$k^* = k_s e^{-i\delta} (\cos \delta - i \sin \delta) \quad (2.13)$$

where  $k_s = D_0 / E_0$  is the static dielectric constant. In term of a complex dielectric constant

$$k^* = k' - ik'' = \frac{\epsilon^*}{\epsilon_0} = \frac{1}{\epsilon_0} (\epsilon' - i\epsilon'') \quad (2.14)$$

From equation (2.13) and (2.14), one obtains

$$k'' = k_s \sin \delta \quad (2.15)$$

$$k' = k_s \cos \delta \quad (2.16)$$

The loss tangent can be defined as the ratio of equation (2.15) and equation (2.16).

$$\tan \delta = \frac{k''}{k'} = \frac{\epsilon''}{\epsilon'} \quad (2.17)$$

Alternatively, loss tangent ( $\tan \delta$ ) is also known as the dissipation factor ( $D$ ). The inverse of  $\tan \delta$  is commonly used as a figure of merit known as the quality factor ( $Q$ ).