



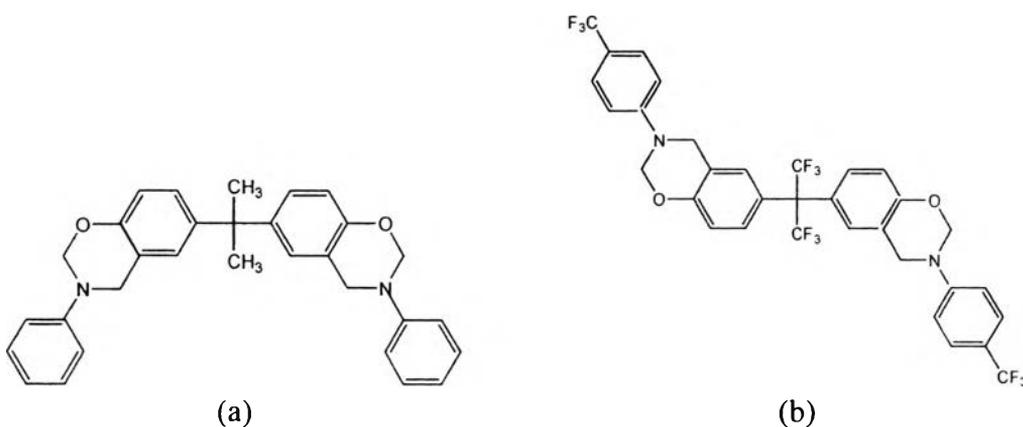
## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Polybenzoxazine

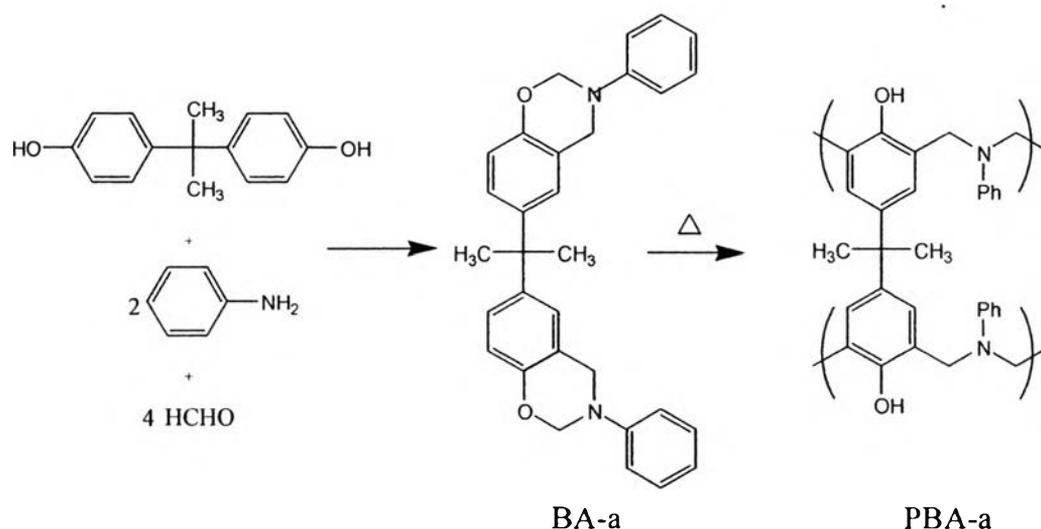
Polybenzoxazines are a new class of thermosetting polymers being developed as an alternative to the traditional phenolics. The novel materials provide characteristics found in the conventional phenolic resins, such as high heat resistance and flame retardance. They also provide features that are not found in the conventional ones, such as excellent dimensional stability, low water absorption, high char yield, good electrical properties, and wide molecular design flexibility (Ning and Ishida, 1994). Moreover the polymerization of polybenzoxazines can be done with no strong acid or alkaline catalysts requirements, and no by-products are generated during the reaction. Therefore, they are widely used in various fields like electronics and aerospace industries.

A series of polybenzoxazines is obtained by the ring-opening polymerization of benzoxazine monomers. A benzoxazine monomer is a single benzene ring fused to another six-membered heterocycle containing one oxygen atom, and a single nitrogen atom as shown in Figure 2.1. There are a number of possible isomeric benzoxazines, depending on the relative positions of the two heteroatoms and the degrees of oxidation of this oxazine ring system.



**Figure 2.1** The structures of benzoxazine monomers; (a) aniline-based benzoxazine and (b) fluorinate-based benzoxazine.

Benzoxazine monomers were first synthesized by Holly and Cope in 1944, prepared from the Mannich reaction of phenols, primary amines, and formaldehyde. The molecular design flexibility of monomers can be performed by the variation of the phenols and amines derivative. The polymerization occurs through the ring-opening polymerization of the cyclic at high temperatures in the absence of a catalyst and without generating any by-products. For the polymerization reaction, Burke *et al.* (1949) found that benzoxazine monomers react almost specifically with the ortho position of a phenol compound to form a methylene-amine-methylene bridge structure in the polymer. In the past, all benzoxazine studies were reported using preformed benzoxazine monomers as the precursor for the polymerized benzoxazines. It has been reported that monofunctional benzoxazine molecules do not form large molecular weight polymers, despite the possibility of forming a linear polymer (Reiss *et al.*, 1985). Later, this problem could be overcome when Ning and Ishida (1994) discovered that only difunctional or multifunctional benzoxazines can offer the crosslink structure which makes polybenzoxazines possess excellent mechanical properties and high glass transition temperatures. An example of the reaction for benzoxazine monomer preparation and the resulting polybenzoxazine is shown in Figure 2.2.



**Figure 2.2** Synthesis of benzoxazine monomer (BA-a) and polybenzoxazine (PBA-a) prepared from bisphenol A, aniline, and formaldehyde.

In 1995, Ishida and Rodriguez studied the curing mechanism of benzoxazine precursors based on bisphenol A and aniline by using differential scanning calorimetry. They found that benzoxazine precursors undergo an autocatalytic-type curing mechanism and that further structural rearrangements may be occurring at high temperatures during the curing reaction. Then Ishida and D.J.Allen, 1996, synthesized polybenzoxazine precursors derived from bisphenol A-aniline based and bisphenol A-methylamine based benzoxazine monomers. From the mechanical and physical characterization, they found that the two phenolic polybenzoxazines materials exhibited high temperature, high strength matrix materials. Dynamic analysis reveals that these candidates for composite applications possess high moduli and glass transition temperature, but low crosslink densities. In addition, they also showed that these new materials were able to perform in electrical applications as well as conventional phenolic and epoxy resins due to their low water absorption and good dielectric properties.

As we know, there are several choices of phenols and amines for the synthesis of benzoxazine monomers. Hence, polybenzoxazines can be addressed in many fields, including in electronics applications. In 2003, Su and Chang prepared polybenzoxazine with low dielectric constant for use as insulating materials. In their study, a novel structure of the fluorinated benzoxazine was synthesized by incorporating the trifluoromethyl groups into the monomer. Further, they prepared the fluorinated copolybenzoxazine with different ratios of bisphenol A-aniline based benzoxazine (BA-a) and fluorinated based benzoxazine (F-1). The characterizations showed that the incorporation of fluorinated substitution results in decreasing the dielectric constant with a tolerable dissipation factor; the co- polybenzoxazine with BA-a/F-1 gives a low dielectric constant at 2.36 and  $\tan \delta$  at 0.0044 (at 1 MHz), which is suitable for insulating applications. Next, Su *et al.* (2005) studied the morphologies and dielectric constants of poly( $\epsilon$ -caprolactone)/polybenzoxazine copolymers. The co-polymers were prepared by treating various molecular weights of poly( $\epsilon$ -caprolactone) (pa-PCL) with BA-a type polybenzoxazine, which act as the labile and stable constituents, respectively. Then, the porous structures were obtained by dissolving the mixture in THF and evaporating it during curing. Lastly, they concluded that the labile polymer micro-phase separates in the polybenzoxazine

matrix with domain sizes that depend on the molecular weight of the pa-PCL used. These porous materials have dielectric constants, relative to that of the virgin polybenzoxazine (3.56), that are as low as 1.95 at  $10^5$  Hz and 298 K.

According to the development of polybenzoxazines that combined the thermal properties and flame retardance of phenolics with the mechanical performance of advanced epoxy systems (Ishida and D.J.Allen, 1996) so they have been interested in composite applications. In 1996, polybenzoxazines were successfully cured with carbon fiber by Shen and Ishida. The obtained composites show good mechanical and physical properties compatible with polyimide composites and bismaleimide composites.

However, there are some disadvantages for polybenzoxazines, such as the brittleness of the cured resin, the relative high temperature needed for the ring-opening polymerization, and the low storage modulus at  $T_g$  due to low crosslink density. Therefore, the enhancement of thermal and mechanical properties for typical polybenzoxazine is expected. There are various approaches that have been developed, including the hybridization of typical benzoxazine monomers with nanosized inorganics for example; Agag and Takeichi (2000) synthesized a novel polybenzoxazine-montmorillonite hybrid nanocomposite. Due to the nanoscale dispersion of silicate layers of clay, they found that the composite shows the enhancement in the thermal stability compared with virgin polybenzoxazine. Moreover, Agag *et al.* (2004) improved polybenzoxazine by preparing a polybenzoxazine-titania hybrid nanocomposite that shows increasing thermal stability and char yield performance.

## 2.2 Dielectric Properties

Dielectric constant of material is strongly influenced by polarization of the molecule as shown in the Clausius-Mossotti relationship:

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M_w}{\rho} = \frac{N_A \alpha}{3 \epsilon_0} \quad (2.1)$$

where  $\epsilon$  is dielectric constant,  $\alpha$  is total polarizability

From the relationship, it can be seen that as the total polarizability increases, the dielectric constant also increases. In polymeric materials there are three modes of polarization which contribute to the total polarization.

(a) *Electronic polarization* ( $\alpha_e$ ): an electric field will cause a slight displacement of the electrons of any atom with respect to the positive nucleus. Since only the movement of electrons is involved, this process can occur very rapidly and typically has a time constant of around  $10^{-15}$  s.

(b) *Atomic polarization* ( $\alpha_a$ ): results from rearrangement of nuclei in response to an electric field. The positive nuclei are attracted to the negative pole of the applied field. However, the movement of heavy nuclei is more difficult to initiate and reverse than that of electrons and so cannot follow an oscillating field at as high a frequency as electronic polarization.

(c) *Dipole orientation polarization* ( $\alpha_o$ ): if the molecules already possess permanent dipole moments, there is a tendency for these to be aligned by the applied field to give a net polarization in that direction. However, the orientation of molecular dipoles can make a contribution which is large, but which may be slow to develop, to the total polarization of a material in an applied field. In solid polymers, dipole movement is usually restricted then it becomes less significant than the electronic mode.

Thus equation (2.1) becomes as equation (2.2):

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M_w}{\rho} = \frac{N_A (\alpha_e + \alpha_a + \alpha_o)}{3 \epsilon_0} \quad (2.2)$$

From equation (2.2), it can be observed that the dielectric constant will always scale with the polarizability. The greater the sum of the three modes of polarization, the

greater the dielectric constant will be. Because of the different time constants of the three modes of polarization, it follows that the dielectric constant will be frequency dependent.

At optical frequencies, where only electronic polarization is occurring, the dielectric constant can be found by the application of Maxwell's identity, shown in equation 2.3.

$$\epsilon = n^2 \quad (2.3)$$

where  $n$  is the refractive index refers to at optical frequencies. Then substitute (2.3) into (2.2) gives a quantity called the molar refraction of the material:

$$\frac{n^2-1}{n^2+2} \frac{M_w}{\rho} = \frac{N_A (\alpha_e + \alpha_a + \alpha_o)}{3 \epsilon_0} \quad (2.4)$$

Equation (2.4) known as, the Lorenz-Lorentz relation, which provides a method of calculating the molecular polarizability from a macroscopic, observed from the refractive index of materials.

The dielectric loss relates to the polarization and current in an alternating field. When an alternating current is applied to a sample, if the frequency is high enough, the orientation of any dipoles which are present will inevitably lag behind the applied field, giving rise to energy dissipation (such an effect is called dielectric relaxation). Mathematically express this as a phase lag  $\delta$  in the electric displacement:

$$D = D_0 \cos(\omega t - \delta) \quad (2.5)$$

which may be written

$$D = D_1 \cos\omega t + D_2 \sin\omega t \quad (2.6)$$

where

$$D_1 = D_0 \cos \delta \text{ and } D_2 = D_0 \sin \delta$$

And an alternating electric field  $E$ , amplitude  $E_0$  and angular frequency  $\omega$  is

$$E = E_0 \cos\omega t \quad (2.7)$$

This leads to define two relative permittivities

$$\epsilon' = \frac{D_1}{\epsilon_0 E_0} \quad \text{and} \quad \epsilon'' = \frac{D_2}{\epsilon_0 E_0} \quad (2.8)$$

The loss tangent can then be defined as

$$\frac{\epsilon''}{\epsilon'} = \tan \delta \quad (2.9)$$

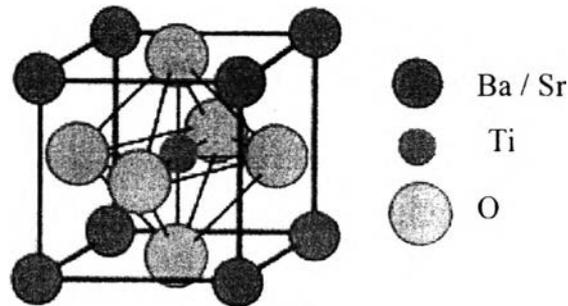
$\epsilon''$  is called the dielectric loss factor and  $\tan \delta$  is usually called the dielectric loss tangent or dissipation factor.

### 2.3 Barium Strontium Titanate

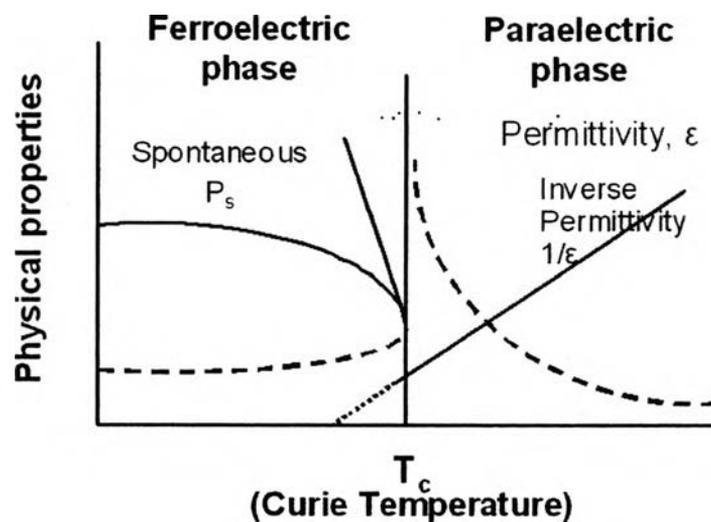
Barium strontium titanate (BST) is a well-known ferroelectric ceramic material, which has been extensively investigated in the last 50 years because of its various applications in electronic devices. It is a suitable dielectric material for the applications of microelectronic devices such as dynamic random access memories (DRAMs), bypass capacitors, IR detectors, and microwave devices owing to its high dielectric constant, low dielectric loss, good thermal stability, and high frequency characteristics (Lin *et al.*, 2005).

Perovskite barium strontium titanate (BST,  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ), as shown in Figure 2.3, is a general class of ferroelectric materials which is derived from barium titanate ( $\text{BaTiO}_3$ ). Barium titanate ceramics show good dielectric properties and have been extensively used in high dielectric capacitors. It was noted that ceramics will show the highest permittivity or dielectric constant at Curie temperature,  $T_c$  (the temperature at which the ceramics exhibit a ferroelectric-paraelectric phase transition (tetragonal-cubic)), as shown in Figure 2.4. The Curie temperature of barium titanate is  $130^\circ\text{C}$ , which limits its use as high dielectric capacitors at room temperature. However, the Curie temperature of barium titanate can be decreased linearly by the substitution of strontium for barium to form barium strontium titanate (BST,  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ). In addition, for a barium-rich composition ( $x < 0.35$ ), BST is ferroelectric at room temperature. As strontium molar fraction increase, the Curie temperature of BST shifts to lower room temperature. According to this way, BST can be a paraelectric at room temperature to perform a high dielectric constant, low tangent loss, and large dielectric breakdown strength (Lu *et al.*, 2003). However, the dielectric properties of

BST ceramics are also affected by the microstructure, such as size and shape of grains (Swartz, 1990).



**Figure 2.3** A cubic perovskite  $ABO_3$ -type unit cell of  $Ba_{1-x}Sr_xTiO_3$  (Lu *et al.*, 2003).



**Figure 2.4** First-order phase transition in a ferroelectric (Uchino K., 2000).

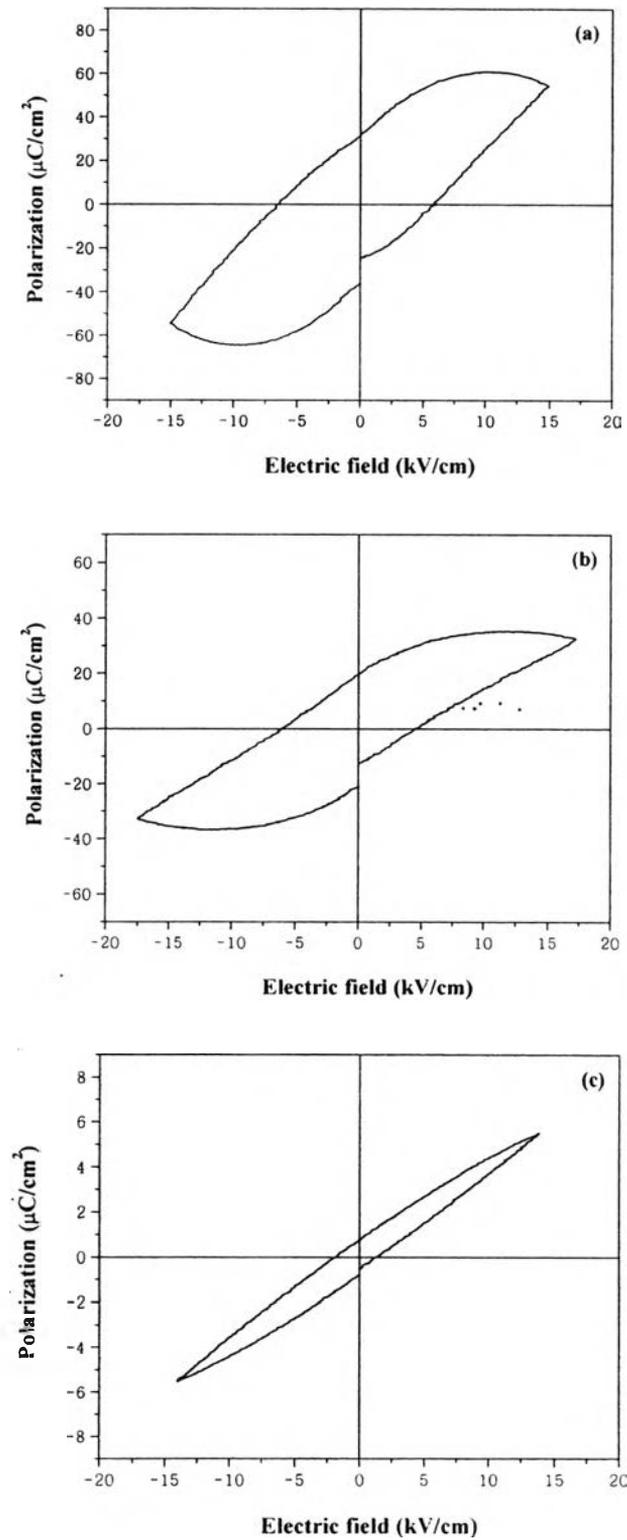
Presently, BST powders are widely synthesized by the sol-gel method because it provides powders with high chemical purity and homogeneity through a lower temperature process, grain size and shape control, and the avoidance of contamination of the materials. It also yields better stoichiometric control and nanopowder with high sinterability (Yang *et al.*, 2003).

According to the previous thesis work of Panomsuwan G., nano-sized BST powder was synthesized by using the sol-gel method and studied the effect of  $Sr^{2+}$

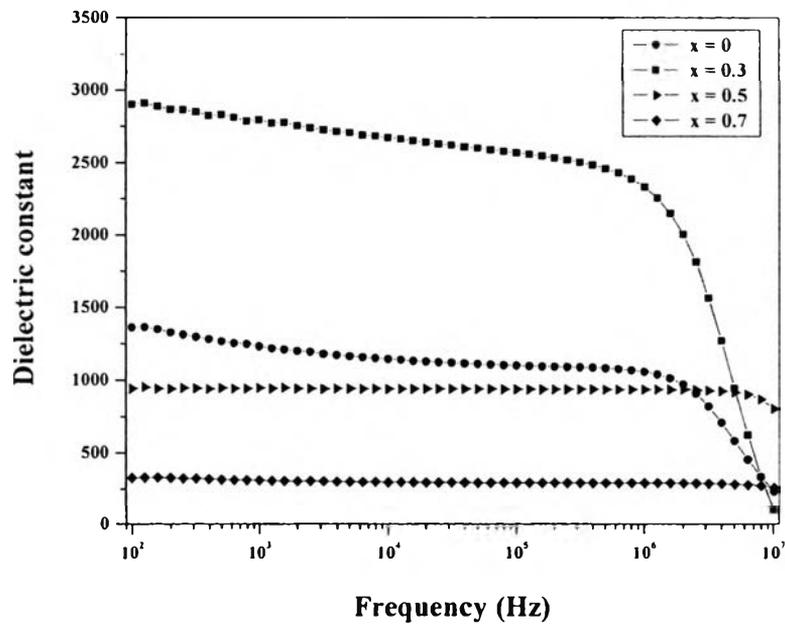
into  $\text{Ba}^{2+}$  on the microstructure, and the dielectric properties of BST ceramics. The molar fraction ( $x$ ) of strontium was varied by  $x = 0, 0.3, 0.5,$  and  $0.7$  to adjust the Curie temperature and obtained BST ceramics in paraelectric and ferroelectric phase at room temperature. From the results, he found that all of the BST particles had an average size of around 50 nm in diameter, with a uniform distribution in size and shape. From XRD characterization, at calcination temperature of  $800^\circ\text{C}$ , there are some undesirable phases, including  $\text{Ba}(\text{Sr})\text{TiO}_3$  and  $(\text{Ba},\text{Sr})_2\text{Ti}_2\text{O}_5\text{CO}_3$  as incorporated strontium. To solve this problem, an increase in the calcination temperature was introduced. Moreover, the structure of the sol-gel powders at all compositions was cubic phase until after the sintering process. BST ceramics at  $x = 0$  and  $0.3$  change to tetragonal structure while the ceramics with  $x = 0.5$  and  $0.7$  still exist in cubic structure. Also the SEM images showed that the BST ceramics at all compositions possess uniform grain sizes when the sintering temperature was  $1400^\circ\text{C}$ .

Panomswan G. also studied the ferroelectric and paraelectric behavior of the  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  from the relationship between polarization ( $P$ ) and electric field ( $E$ ) at room temperature, as shown in Figure 2.5. He found that the hysteresis loop of BST ceramics can be observed with  $x = 0$  and  $0.3$ , which shows the characteristic ferroelectric behavior, while the strontium fraction of  $0.5$  and  $0.7$  shows a more linearly relation between polarization and electric field that indicates the paraelectric feature. From the dielectric properties of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ , as shown in Figure 2.6 and Figure 2.7, BST with a strontium fraction of  $0.3$  shows the highest dielectric constant ( $\sim 2700$ ) at room temperature. But this value drops rapidly at high frequency ( $>1$  MHz) while the dielectric loss increases abruptly due to the dipolar relaxation. Although the dielectric constants of the BST ceramics with  $x = 0.5$  and  $0.7$  are lower than those with  $x = 0$  and  $0.3$ , they show lower dielectric loss at that high frequency.

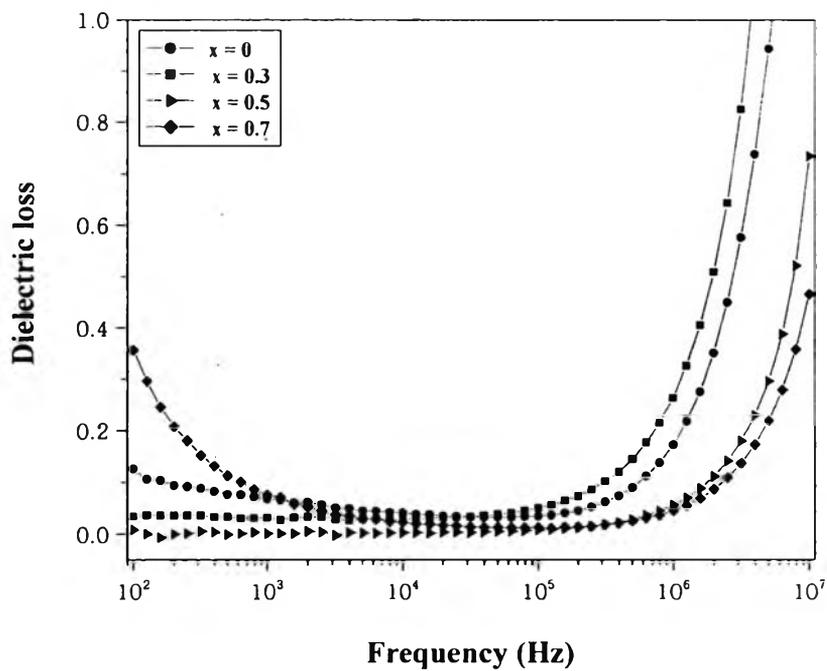
It is known that at high frequency, ferroelectric ceramics typically undergo a relaxation in their dielectric properties, which in turn leads to a decrease in relative permittivity with frequency (Pant *et al.*, 2006). Thus the dielectric properties of materials working at high frequencies are very important, especially the dielectric loss that is required to be as low as possible. According to the work of Panomswan G. the BST ceramic with a strontium fraction of  $0.7$  shows the lowest dielectric loss. Therefore,  $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$  was selected for study in this thesis work.



**Figure 2.5** Hysteresis loop of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ceramics at room temperature: (a)  $x = 0$ , (b)  $x = 0.3$ , and (c)  $x = 0.5$  (Panomsuwan G., 2006).



**Figure 2.6** Dielectric constants of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ceramics at room temperature (Panomsuwan G., 2006).

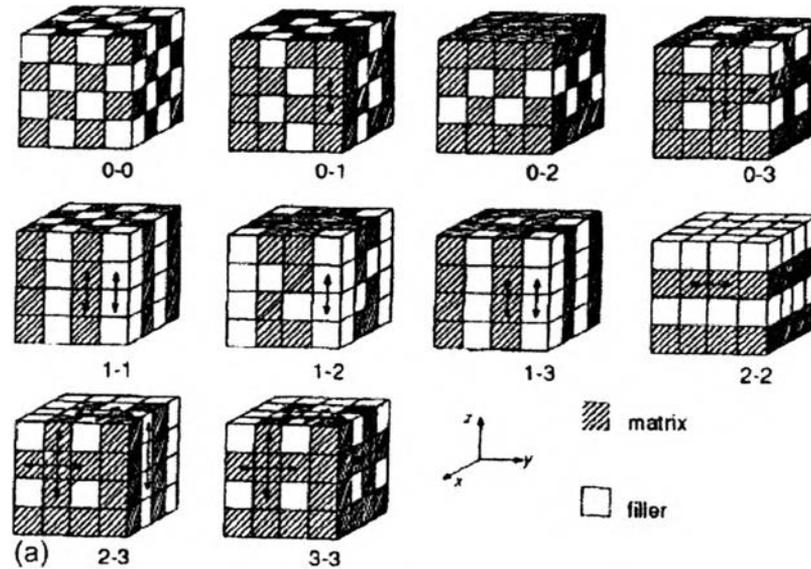


**Figure 2.7** Dielectric losses of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ceramics at room temperature (Panomsuwan G., 2006).

## 2.4 Polymer-Ceramic Composite

Nowadays, there is an increasing demand for the use embedded capacitors working at multi frequencies, particularly at high frequencies. The required properties of these materials are that they possess frequency-independent permittivities, low dielectric loss, good processability, and low cost (Pant *et al.*, 2006). Polymers are flexible, easy to process with low processing temperature, and possess a high dielectric breakdown field; but generally suffer from low dielectric constant. On the other hand, ceramics possess a very high dielectric constant, but they are brittle, require high temperature processing, and have low dielectric strength. Integrating these two materials results in a new material with high dielectric constant, high breakdown field, and ease of processing to achieve high volume efficiency and energy storage density for applications of capacitors (Bai *et al.*, 2000).

Polymer-ceramic composites can be designed into ten connectivity patterns which are 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, and 3-3, as shown in Figure 2.8. Among these patterns, the simplest type is 0-3 connectivity, which consists of a three dimensionally connected polymer matrix loaded with ceramic particles. The major advantages of the 0-3 type are its versatility in a variety of forms, including thin sheets and certain molded shapes. This type of composite is also easy to fabricate and is amenable to mass production (Lee *et al.*, 1989).

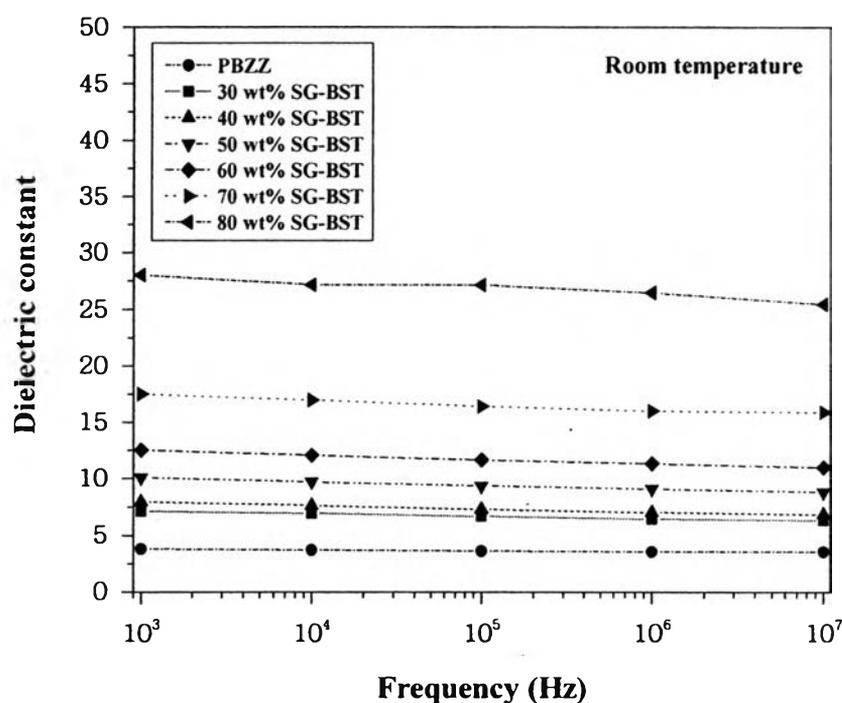


**Figure 2.8** Connectivity patterns in a diphasic composite system (Lee *et al.*, 1989).

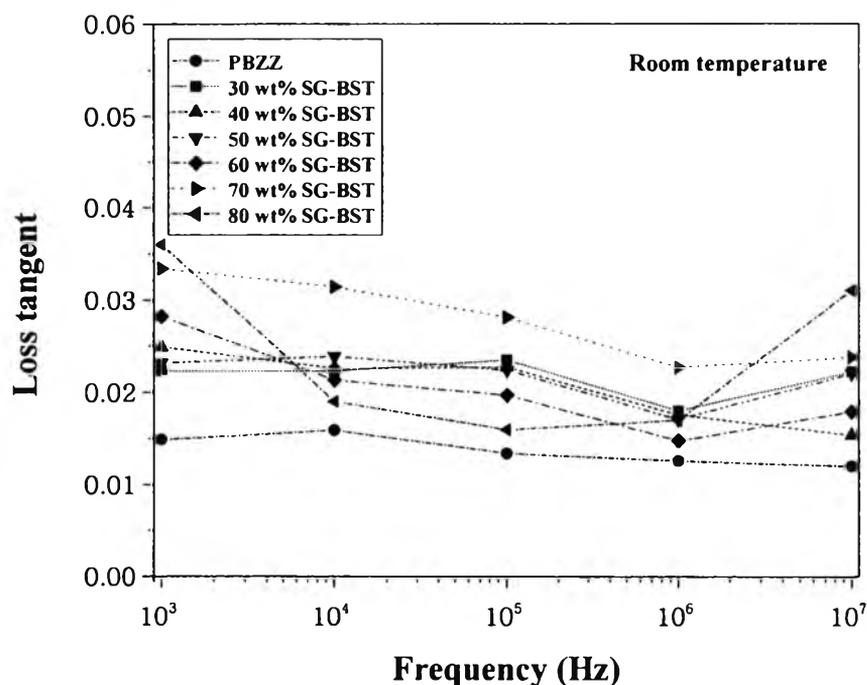
In order to produce the composite materials for high frequency applications, the composites must exhibit high permittivity with low dielectric loss. There are many research works that studied the dielectric behavior of 0-3 composites with different types of polymer matrices and ceramic fillers. BST is one type of ferroelectric ceramic that is widely used as a ceramic filler, due to its high dielectric constant and low loss properties at room temperature. Thermosetting polymers including epoxy, polyimide, and polyurethane are generally used as the polymer matrix in composites for electronic devices, especially embedded capacitor applications because they are compatible with print circuited wiring board (PWB) and provide good thermal stability and electronic properties (Kuo *et al.*, 2000). However, among the previous works, there is nothing reported on the study of dielectric properties of polybenzoxazines-BST ceramics composite, until Panomsuwan G. (2006) investigated the novel polybenzoxazine-BST composite with 0-3 connectivity.

In his work, sol-gel  $\text{BaTiO}_3$  powders, sintered  $\text{BaTiO}_3$  powders, and sol gel  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  powder were used as the ceramic fillers, and polybenzoxazine based on phenol, paraformaldehyde, and ethylenediamine was used as the polymer matrix. The ceramic powders were added to the benzoxazine monomer powder in the amount of 30, 40, 50, 60, 70 and 80wt%. Then, composite specimens were prepared by

compression molding. From the SEM image, some agglomerations of ceramic occurring within the composites were observed. The dielectric measurement of the composites revealed that the dielectric constants of all composites are weakly dependent on frequency (1 kHz – 10 MHz) and higher ceramic content leads to a higher composite dielectric constant. It also showed that the composites with 80wt% of sol gel  $Ba_{0.7}Sr_{0.3}TiO_3$  powder provides the highest dielectric constant, 28 (at 1 kHz and tends to be lower at high frequency), which is greater than pure polybenzoxazine by around four times, and provides the dielectric loss of about 0.05. The dielectric constant and dielectric loss of the composite with sol-gel  $Ba_{0.7}Sr_{0.3}TiO_3$  powder are shown in Figure 2.9 and Figure 2.10, respectively.



**Figure 2.9** Frequency dependence of dielectric constant of the composite at various sol-gel BST (SG-BST) contents (Panomsuwan *et al.*, 2006).



**Figure 2.10** Frequency dependence of dielectric loss of the composite at various sol-gel BST (SG-BST) contents (Panomsuwan *et al.*, 2006).

From the effort of Panomsuwan G., it was known that a novel polybenzoxazine-BST composite with 0-3 connectivity can be applied in electronic applications due to its moderate high dielectric constant and low dielectric loss, in the 1 kHz – 10 MHz range.

Although this composite material provided a good dielectric behavior at low frequency, its dielectric constant and dielectric loss tended to decrease and increase at higher frequency, respectively. Therefore, this material is still not good enough for use at high frequency, compared with the commercial composites. Thus the objective of this research is to improve the dielectric behavior of this novel material in order to push it to be one of the commercial composites.

Generally, the dielectric properties of polymer-ceramic composites are strongly influenced by the loading volume and dispersion of the ceramic fillers (Dias and Das-Gupta, 1996). In order to achieve a high dielectric constant, the increase of ceramic loading is normally used. In addition, the amount of filler has to be more than 30 vol% in order to change the permittivity of the composite, but should not exceed

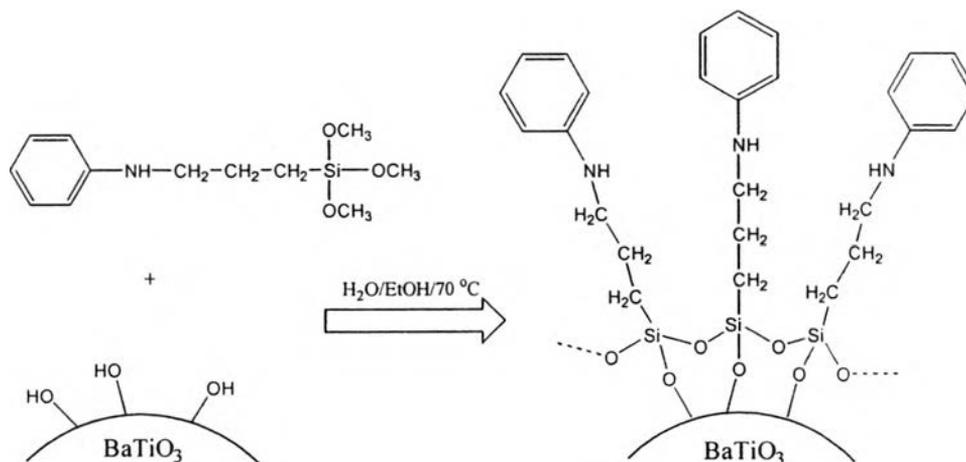
80 vol% because this level may reduce the processability of the material (Rao *et al.*, 2002). However, a common problem associated with the polymer-ceramic composites is the incompatibility of the two materials. When these different materials are mixed, the ceramic particles tend to agglomerate and separate from the polymer matrix, as illustrated in Figure 2.11, resulting in an increase of dielectric loss of the material.



**Figure 2.11** Agglomeration and dispersion of ceramic particles into polymer matrix (Liang *et al.*, 1998).

It was found that the surface treatment of ceramic particles is one effective method to achieve a high dielectric constant of the composites by improving the ceramic dispersion. Previously, many researchers have studied the effect of dispersants on the dielectric properties of the composites. The dispersant which is widely used in this field is silane coupling agents.

Silane coupling agents can provide an effective method to form good compatibility between ceramic fillers and polymer, because they not only adsorb in a single layer on the ceramic surface but also react with the polymer to form an interphase layer between them. Thus good dispersion of the ceramic occurs which will increase the dielectric constant of the composites (Dang *et al.*, 2006). The surface treatment of ceramic particles with silane coupling agents is illustrated in Figure 2.12.

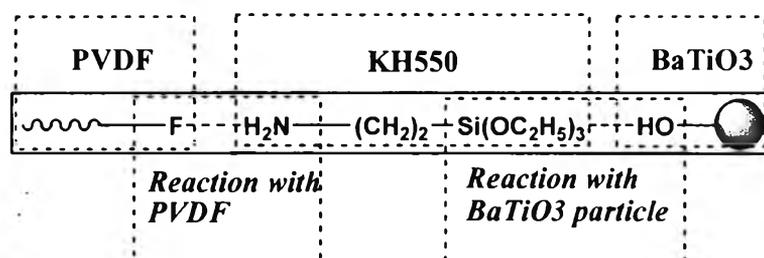


**Figure 2.12** Surface treatment of BaTiO<sub>3</sub> with N-phenylaminopropyltrimethoxysilane (Liang *et al.*, 1998).

Liang *et al.* (1998) prepared a BaTiO<sub>3</sub>-epoxy composite for use as integrated thin film capacitors. Before dispersing the BaTiO<sub>3</sub> powders into epoxy, they modified the BaTiO<sub>3</sub> particles with N-phenylaminopropyltrimethoxysilane to obtain silylate BaTiO<sub>3</sub> powders first. The effects of silane functionalization on the dispersion of BaTiO<sub>3</sub> were examined by sedimentation experiments in various organic solvents. The results showed that the dispersion process depends on both the surface modification and the organic system. In this case, the modified BaTiO<sub>3</sub> particles dispersed very well in NMP and methylethylketone, which are commonly used in epoxy and polyimide formulations. Then a thin film composite with modified BaTiO<sub>3</sub> was fabricated and the dielectric properties were then measured. A dielectric constant of 40 at 1 kHz and a dielectric loss of 0.035 were obtained in the BaTiO<sub>3</sub>-epoxy composite (60/40, v/v).

Dang *et al.* (2006) studied the influence of a silane coupling agent on the morphology and dielectric properties in BaTiO<sub>3</sub>/polyvinylidene fluoride composites.  $\gamma$ -aminopropyltriethoxysilane (KH550) was used as the coupling agent. The powders of BaTiO<sub>3</sub> were chemically modified with KH550 at concentrations of 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0wt% of BaTiO<sub>3</sub> before dispersing into PVDF. Then the composite of BaTiO<sub>3</sub> with 40%vol and PVDF was obtained. The results from SEM showed that the composite with BaTiO<sub>3</sub> modified by 1.0 wt% KH550 displayed a good dispersion of BaTiO<sub>3</sub> without any agglomeration. However, the dispersion and compatibility of

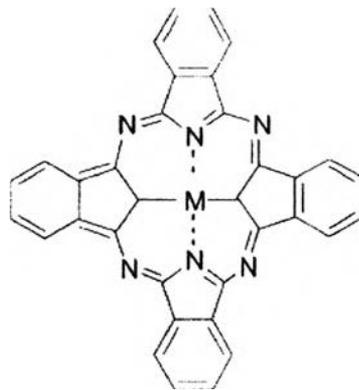
composites are poor when the BaTiO<sub>3</sub> is not modified with KH550 or modified by more than 1.0 wt%, which show many more pores and polymer aggregation. From IR spectra, they suggested that KH550 can act as bridge-linked action to bind the BaTiO<sub>3</sub> with PVDF, as shown in Figure 2.13.



**Figure 2.13** Chemical reaction process of KH550 with both surface of BaTiO<sub>3</sub> and PVDF (Dang *et al.*, 2006).

From the dielectric measurement, they proved that dielectric constants of the composites with BaTiO<sub>3</sub> treated by less or more 1.0 wt % KH550 are almost the same as that of the composite with raw BaTiO<sub>3</sub>. On the other hand, the dielectric constant of the composite with BaTiO<sub>3</sub> modified by 1.0 wt % KH550 can be improved about 20% in comparison to the composite with raw BaTiO<sub>3</sub> without KH550 at a frequency from 10<sup>3</sup> to 10<sup>5</sup> Hz. Moreover, they also found that the dielectric loss of the composite with KH550 is less than 0.05 below 10<sup>5</sup> Hz, which shows that this material has a potential application as dielectric in capacitor.

Phthalocyanines (Pc) have been one of the most studied classes of organic functional materials, especially as a candidate for organic semiconductor materials applied to organic transistors, chemical sensors, and organic electro luminescent devices (Li Li *et al.*, 2005). Its molecule is able to coordinate hydrogen and metal cations in its center by coordinate bonds with the four isoindole nitrogen atoms, as shown in Figure 2.14. The central atoms can carry additional ligands. It was found that Cu-Pc oligomers can provide a dielectric constant as high as 100,000. The large dielectric can be explained in terms of the electro delocalization within the metal-Pc molecules.



**Figure 2.14** Structure of phthalocyanine (Pc) (Li Li *et al.* (2005).

Li Li *et al.* (2005) tried to improve the dielectric property of epoxy-BaTiO<sub>3</sub> composite for embedded capacitor application by treating the surface of BaTiO<sub>3</sub> with phthalocyanine. They believed that phthalocyanine might form with the barium and titanium ions (Ba-Pc and Ti-Pc) on the surrounding surface of BaTiO<sub>3</sub> particles. Then good dispersion of BaTiO<sub>3</sub> in matrix and high dielectric constant could be obtained. From the dielectric measurement, the dielectric constant of polyamide-Pc coated BaTiO<sub>3</sub> composite film increased dramatically as they expected. The composite showed a dielectric constant of 80 and a dielectric loss of 0.03 at 1 MHz with a BaTiO<sub>3</sub> loading ratio of 70 vol%, which was much higher than that of the composite derived from commercial BaTiO<sub>3</sub>.

However, there are some articles reporting about coating benzoxazine monomer on the fillers in the composites derived from polybenzoxazines. Huang *et al.* (1999) were able to fabricate a polybenzoxazine-benzoxazine coated boron nitride composite. The benzoxazine coated boron nitride particles were prepared by dissolving the appropriate amounts of the purified benzoxazine monomer in THF, then adding into boron nitride particles. Various surface coating thicknesses on the particles were obtained by varying the benzoxazine solution concentrations. So this method is another interesting approach to prevent the agglomeration of ceramic fillers in polybenzoxazine matrix that may increase dielectric loss in the composites.