CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Polybenzoxazine in Electronic Application

The phenolic resins are widely used in various applications, from commodity and construction materials to the needs of the high technology aerospace industry. Recently, a new type of addition-cure phenolic family, polybenzoxazine, has been developed. Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached as shown in Figure 2.1. The polybenzoxazine have many advantageous characteristics compared with the traditional phenolic resins, such as high thermal stability and excellent mechanical properties, easy processibility, low water absorption, near zero shrinkage after polymerization, excellent molecular design flow water, excellent electrical properties, high char yield, no strong acid catalysts required for curing, release of no by-products (even nontoxic) during polymerization, low coefficient of thermal expansion (CTE) and for some polybenzoxazine based materials glass transition temperature (T_g) much higher than cure temperature (Ghosh et al.,2007).
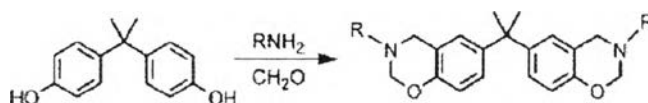

Figure 2.1 Synthesis of the bisbenzoxazine monomer (Ning et al., 1994).

The benzoxazines were first synthesized by Cope and Holy in 1940s via Mannich condensation reaction of primary amines with formaldehyde and substituted phenols and this reaction was performed in a solvent in two-steps. Later, Burke found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge ($-CH_2-N(R)-CH_2-$) (Bruke et

al.,1949).Until in 1973, the benzoxazine was well-known as the kind of phenolic resin precursors by Scheriber. He reported the hard and brittle phenolic resin was formed from benzoxazine precursors. The use of an organic solvent also leads to problems during processing of the benzoxazine resins moreover, also increases the cost of the products and causes environmental problems. So, Ishida *et al.* developed a solventless synthesis in the melt state in order to overcome these shortcomings (Ishida, 1994). Next, Liu J. (1995) was proposed the reaction mechanism and kinetics of this solventless synthesis. In a typical synthesis, the reactants are physically mixed together, heated to their melting temperature, and then kept their up at a high enough temperature to complete the interaction of the reactants finally, benzoxazine was desired. In this connection, paraformaldehyde is used instead for formaldehyde because it evaporates easily and loses stoichiometry quickly. In addition, the variation of the phenols and amines derivative can be provides the flexibility in designing monomer structure.

Generally, the properties of the polybenzoxazine materials is developed by various methods. the preparation of novel monomers, copolymers, polymer alloys, and fiber reinforced composites, that become increasingly attractive to overcome the shortcoming of the typical polybenzoxazines. (Agag *et al.*, 2004)

The benzoxazine-based materials possess excellent mechanical and thermal properties, high dimensional stability, low water absorption, and high char yield, which make benzoxazine a promising matrices candidate for high performance composites, especially in microelectronics, aerospace and packaging industry (Garea *et al.*, 2007). The properties of the polybenzoxazine materials depend on benzoxazine monomer molecular structure and the polymerization processing conditions, and it is essential to understand the polymerization behavior of different benzoxazine resins to define the actual processing conditions. Most research articles were concerned with the study of the popular bisphenol-A based difunctional benzoxazine as shown in Figure 2.2 (Liu *et al.*, 2010).

The polymerization of the bisphenol-A and aniline based benzoxazine (B-a) monomer was studied by using DSC technique by in Ishida *et al.* (1995) as shown in Figure 2.3. They found that until vitrification, the polymerization of benzoxazine precursors is an autocatalyzed reaction is occurred and the diffusion begins to control

the polymerization process. Moreover, during the process those further structural rearrangements may occurring at high temperatures. Next, in 1996 Ishida and D.J. Allen, the polybenzoxazine precursor was synthesized by using bisphenol-A, formaldehyde, aniline and methylamine in different solvents which are bisphenol A-aniline based and bisphenol A- methylamine based benzoxazine monomers. The mechanical and physical properties of these two phenolic polybenzoxazines were studied that showed high temperature, high strength matrix materials. And for the composite application they showed the high moduli and high glass transition temperature but low crosslink densities that can improve by copolymerization with epoxy resins (Ishida H. and Allen D.J. 1996A-1996B).
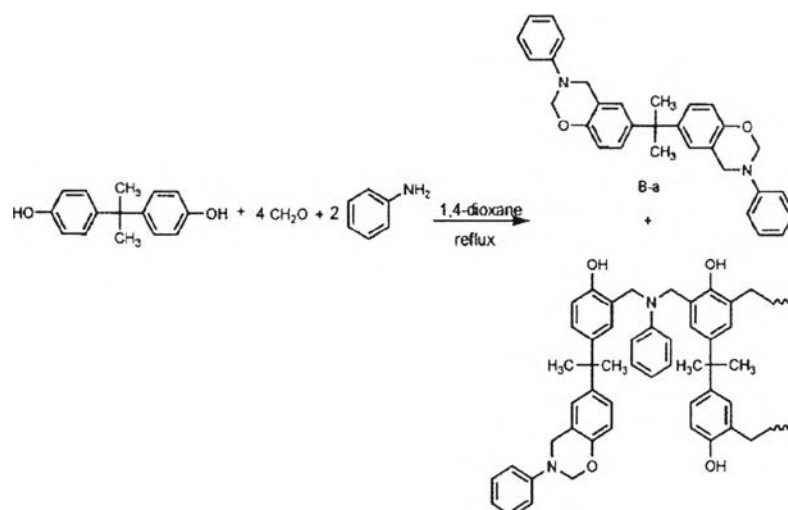

Figure 2.2 Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer (Ghosh *et al.*, 2007).
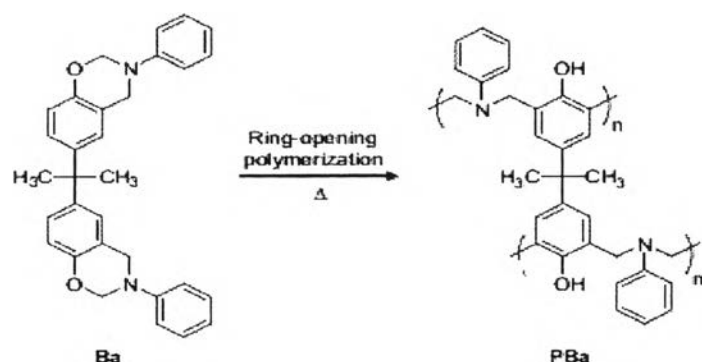

Figure 2.3 Synthesis of polybenzoxazine-anline based (PB-a) (Ardhyananta *et al.*, 2009).

In 1998, Ishida and Rimdusit studied the thermal conductivity of boron nitride-filled polybenzoxazine. They found the thermal conductivity of boron nitride-filled polybenzoxazine exhibited a very high conductivity value. The remarkably high value was obtained using the well-recognized concept of thermal management in composite materials by maximizing the formation of conductive networks while minimizing the thermal barrier resistance along the heat-flow path. The concept was accomplished by using highly thermally conductive filler with a matrix resin which has low melt viscosity and good adhesion to the filler. Boron nitride and polybenzoxazine have properties that meet all these requirements and thus exhibit a very high thermal conductivity value. This molding compound also exhibits high and stable mechanical strength up to 200°C with a high T_g value of ca. 220°C. Water absorption at room temperature for 24 h of this composite is very low. Boron nitride-filled polybenzoxazine has many outstanding properties which makes it suitable for an application as a molding compound for the electronic packaging industry and other applications with high thermal conductivity.

In 1999, Kim *et al.*, studied the synthesis and thermal characterization of polybenzoxazines based on acetylene-functional monomers. Their works showed the acetylene functional group polymerization by oxazine ring-opening polymerization forms highly thermally stable cross-linked network. Polymerization in the nitrogen resulted a significant decrease in the degradation temperature as well as the char yield of acetylene functional benzoxazines. Moreover, char formation in the form of mixtures of BA-apa and BA-a confirmed the major contribution of acetylene polymerization to the highly thermally stable structure of BA-apa polybenzoxazine.

Moreover, the hybridization of typical benzoxazine monomers with inorganics nano-particle sizes was studied by Agag and Takeichi (2000). They synthesized a polybenzoxazine-montmorillonite hybrid nanocomposite. Because, the nanoscale dispersion of silicate layers of clay, their study showed the composite have good thermal stability compare with the virgin polybenzoxazine after that in 2004, Agag *et al.* found the polybenzoxazine was improved by using sol-gel process that prepare from polybenzoxazine-titania hybrid nanocomposite. This shows the increasing of thermal stability and char yield performance.

In 2003, Su and Chang studied the synthesis and characterization of fluorinated polybenzoxazine material with low dielectric constant for use as insulating materials. In their study, they synthesized a series of co-PBZZ with different proportion B-a / F-1 ratios. The characterizations show that the fluorination on PBZZ is able to reduce dielectric constant and increase thermal properties. The co-PBZZ with B-a : F-1 = 1 : 1 gives low dielectric constant at 2.36 and tan δ at 0.0044 which is suitable for insulating applications. Moreover, its thermal properties are also substantially improved over the B-a type PBZZ.

In 2005, Takeichi *et al.* studied polymer alloys of polyimide and polybenzoxazine which were prepared from the combination of a bifunctional benzoxazine monomer, 6, 60-(1-methylethylidene) bis (3,4-dihydro-3-2H-1,3-benzoxazine) (B-a) and a soluble polyimide (PI). They found the tensile properties of the PI/B-a films demonstrated that the polyB-a enhanced the modulus of PI, while PI improved the toughness of polyB-a. The thermal stabilities of polyB-a were improved significantly by alloying with PI. The alloying with polyimide is an excellent method to modify the properties of polyB-a, which should be effective for the microelectronic applications. And in 2008, Bismaleimide (BMI) and polybenzoxazine was used as the polymer alloys that exhibit the T_g of the polymer alloys shifted to higher temperature by increasing the BMI content. In particular, the T_g of the polymer alloys at high BMI contents were even higher than those of each resin due to the formation of AB co-cross-linking. The thermal stability also increased with the increase of BMI content as evidenced by TGA. The polymer alloys developed in this study can be good candidates for the matrix resin of advanced composite materials and also for the rigid printed circuits because of the excellent high temperature properties.

In 2005, Su. and coworker studied the morphologies and dielectric constants of poly (ε-caprolactone)/polybenzoxazine co-polymers. The co-polymers were prepared by treating various molecular weights of poly (ε-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 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 as 1.95 that lower than pure polybenzoxazine (3.56) at room temperature and 10^5 Hz.

Krueson N. (2008) synthesized the aniline-based and fluorine based benzoxazine monomer, as shown in Figure 2.4, by solventless method and studied the dielectric properties of benzoxazines at frequency range of 1 kHz-10 MHz and temperature range of 25-200°C.
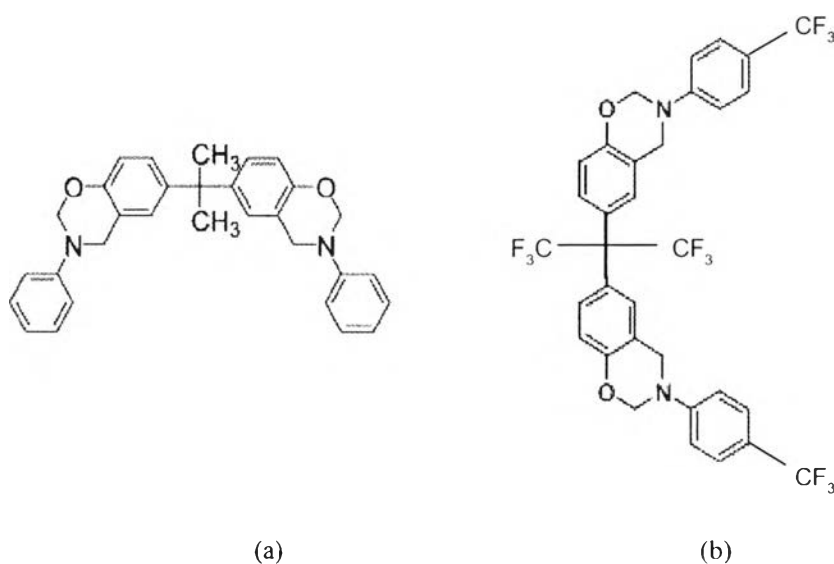

(a)   (b)

Figure 2.4 (a) Aniline-based benzoxazine and (b) Fluorinate-based benzoxazine (Ghosh *et al.*, 2007).

From the results, the dielectric constant of PBA-a and PBA-f were 4.94 and 4.54 at 1 kHz, respectively and nearly stable at 1 kHz-10 MHz while the dielectric loss of PBA-a and PBA-f showed no significant difference at various frequency as shown in Figure 2.5 and Figure 2.6. The positive temperature coefficient (PTC) of dielectric properties was nearly zero in the temperature range of 25-160°C, which indicated the low relaxation behavior.
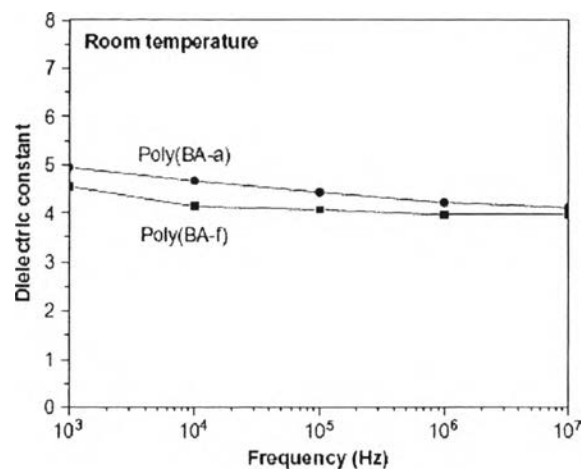
Figure 2.5 The dielectric constant of aniline-based and fluorinate-based poly benzoxazine as a function of frequency (Krueson *et al.*, 2008).
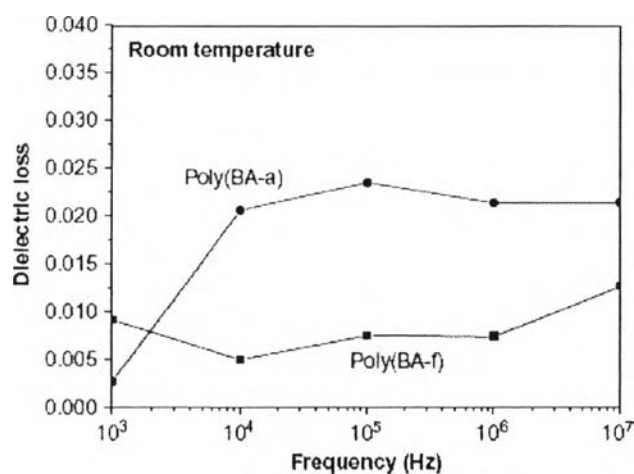

Figure 2.6 The dielectric loss of aniline-based and fluorinate-based polybenzoxazine as a function of frequency (Krueson *et al.*, 2008).

Dielectric properties are affected by the chemical structure of polymers. It was found that the incorporation of fluorinated substitutes into polybenzoxazine was able to reduce dielectric constant and dielectric loss because of small dipole and the low polarizability of C-F bond compared with that of C-H bond. The lower polarizability of C–F bond can induce the hydrophobicity of the polymer. Because the moisture has a very high dielectric constant, it strongly affects the dielectric constant of the polymer. Substitution of hydrogen with F or –CF$_3$ group decreases

the electronic polarizability due to strong electron-withdrawing inductive effect. The bulky $-CF_3$ group is able to reduce efficient molecular packing and increase the free volume. So, more air can be trapped in the polymer chain, resulting in a lower dielectric constant due to the low dielectric constant value of the air (Y.C. Su and F.C. Chang, 2003)

The dielectric properties of aliphatic diamine-based polybenzoxazine were studied by Panomsuwan *et al.* (2007) and the dielectric constant was reported to be 3.81 at 1 kHz that lower than poly(BA-a) and poly(BA-f) of Krueson N.'s result. The lower dielectric constant of the diamine based polybenzoxazine compared with the others is due to the lower number of aromatic rings, as a consequence in lower conjugated double bonds. The polymer that contains more C=C bonds is expected to have a higher relative permittivity or dielectric constant due to the much higher polarizability of the C=C bonds comparing with C-H bonds and C-F bonds.

2.2 Barium Strontium Titanate

Recently, Barium strontium titanate (BST, $Ba_{1-x}Sr_xTiO_3$) ferroelectric ceramic materials have attracted significant interests and are the promising materials for a wide range of applications. In information technology, they are used in DRAM memories (Takasu, 2000). As they present non-linear variation of dielectric constant with the electric field, high dielectric constant and moderate loss in microwave domain, ferroelectric materials present also a high potential for microwave applications. In microwaves, the ferroelectric materials exhibit lower dielectric loss in the paraelectric phase than in the ferroelectric phase. Therefore, most of the electrically controlled devices such as phase-shifters, tunable filters or ferroelectric varactors employ the ferroelectric materials in the paraelectric phase (Ioach *et al.*, 2007).

Perovkite barium stronium titanate (BST, $Ba_{1-x}Sr_xTiO_3$), as shown in Figure 2.7, is a general class of ferroelectric materials which is derived from barium titanate ($BaTiO_3$). Barium titanate ceramics show good dielectric properties and have been extensively used in high dielectric capacitors. It was noted that ceramics will show the hightest dielectric constant at Curie temperature,Tc (the temperature at which the

ceramics show a ferroelectric-paraelectric phase transition (Tetragonal-cubic), as shown in Figure 2.8. The curie temperature of barium titanate is 130°C , which limits its use as high dielecric 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, $Ba_{1-x}Sr_xTiO_3$). 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. Thus, BST can be a paraelectric at room temperature to perfrom a high dielectric constant, low tangent loss, and large dielectric breakdown strength (Lu *et al.*,2003). Furthermore, Ioachim and coworker found that the increasing concentration of Sr has the following effects: (a) decreases considerably the ferroelectric transition temperature; (b) decreases substantially the dielectric constant and losses, for both high and low frequency ranges; and (c) favors the production of BST materials with bimodal grain size distribution (Ioachim *et al.*, 2007). However,the dielectric properties of BST ceramics are also affected by the microstructure, such as size and shape of grains (Swartz,1990)
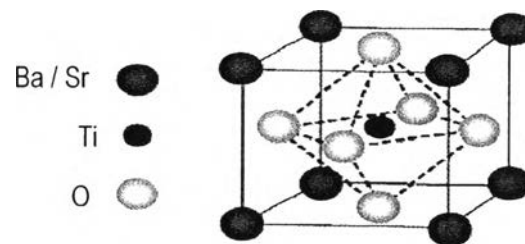

Figure 2.7 Unit cell of Perovkite barium stronium titanate (BST, $Ba_{1-x}Sr_xTiO_3$). (http://www.emg.tu-bs.de/forsch/material/mat_die_en.htm).
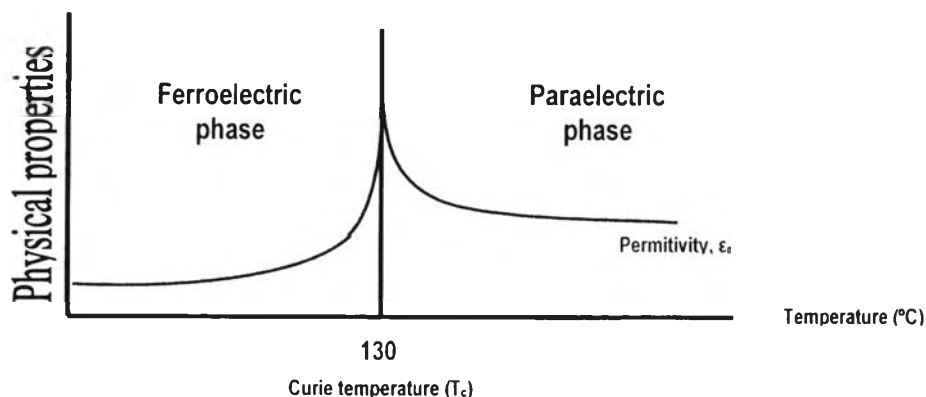

Figure 2.8 Phase transition in Perovkite barium stronium titanate (BST, $Ba_{1-x}Sr_xTiO_3$).

Presently, BST powders are widely synthesized by the sol-gel method becaause it has many attractive advantages which are its versatility and the possibility to obtain high purity and homogeneity materials (shaped as monolithic blocks, powders or thin layers).These occur through a lower temperature process, grain size and shape control, and the avoidance of contamination of the materials. It also yield better soichiometric control and nanopowder with high sinterability(Yang *et al.*,2003).

According to the Panomsuwan G.'s thesis work in 2007, he synthesized the BST powder nano-size by using the sol-gel method and studied the effect of the concentration of strontium on the microstructure and the didelecric properties of this ceamic was studied too. He varied the strontium molar fraction(x) by using x = 0, 0.3,0.5 and 0.7 to adjust the Curie temperature and obtained BST ceramic in paraelectric and ferroelectric phase at room temperature.His result showed that BST particle had uniform distribution in size and shape and an average diameter were around 50 nm.

Beside, he found that after sintering process the structure of sol-gel BST ceramic at x=0 and 0.3 change to tetragonal structure while ceramic with x=0.5 and 0.7 still exist in the same of cubic structure and at sintering temperature was 1400°C the all of BST compositions show uniform grain sizes.

The highest dielectric constant (~2700) was obtained from BST with 0.3 Sr. molefraction at room temperature. However, at 1 MHz and higher, the dielectric constant will drop rapidly meanwhile the dielectric loss increased due to the dipolar relaxation. Although the dielectric constant of BST ceramics with x = 0.5 and 0.7 are lower than those with x = 0 and 0.3, there also show lower dielectric loss at high frequency as shown in Figure 2.9 and 2.10, respectively. The dielectric properties for microelectric device which used in high frequency should be as high as possible. On the other hand, the loss tangent should be as low as possible.

Following previous study, Krueson N.(2008) would choose the BST ceramic with the 0.7 strontium molefraction that exhibits the lower dielectric loss to further development.
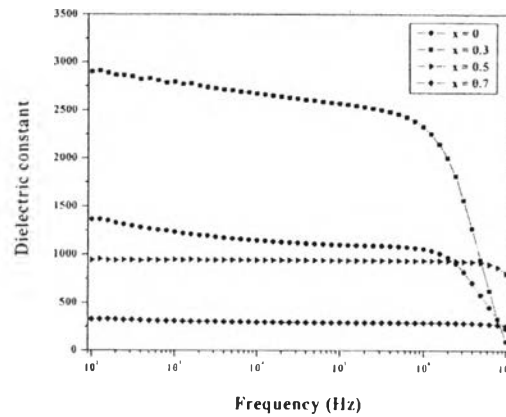
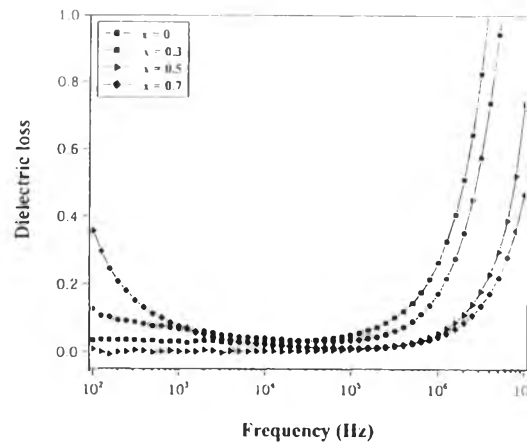**Figure 2.9** Dielectric constants of $Ba_{1-x}Sr_xTiO_3$ ceramics at room temperature (Panomsuwan *et al.*, 2006).

Figure 2.10 Dielectric losses of $Ba_{1-x}Sr_xTiO_3$ ceramics at room temperature (Panomsuwan *et al.*, 2006).

2.3 Polymer-Ceramic Composite

The attractive properties of polymer materials are flexible, easy to process with low processing temperature, and posses a high dielectric breakdown but generally suffer from low dielectric constant while many ceramic materials have the desired high dielectric constant and low dielectric loss, yet they are generally brittle, require high temperature in processing and have low dielectric strength so, in order to overcome that disadvantage the polymer–ceramic composites were prepared (Pant *et al.*, 2006). Polymer–ceramic composites offer excellent materials characteristics

including low temperature processibility, flexibility, high temperature resistance, outstanding solvent resistance etc. One of the most attractive features of filled composites is that their dielectric properties can be varied over a wide range by the choice of the shape, size and connectivity of the constituents in the polymeric matrix (Nisa *et al.*, 2008).

In recent years, polymer–ceramic composites for microelectronics devices especially ferroelectric ceramic–polymer composites have been an important application area. These materials are good candidates for embedded capacitors, capacitive coupled electrical solutions and other integrated high-frequency electronic devices in multilayered structure. (Tao *et al.*, 2007)

As shown in Figure 2.11, there are many conductivity pattern to designed the polymer–ceramic composites which are 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3 and 3-3.From these pattern, the 0-3 pattern is a simplest type of connectivity that consist of a three dimensionally connected polymer matrix loaded whit ceramic particles (Lee *et al.*, 1989). And nowadays, there has been a huge interest in 0–3 ceramic–polymer composites because they enable inexpensive industrial level realization of 3D microwave devices and packages with advanced electric and mechanical properties. Particularly, composites using thermoplastic polymers attract industrial and academic interest because they have the additional advantage of a simple, 3-D fabrication process, such as injection molding of electronic components (Sonoda *et al.*, 2010).
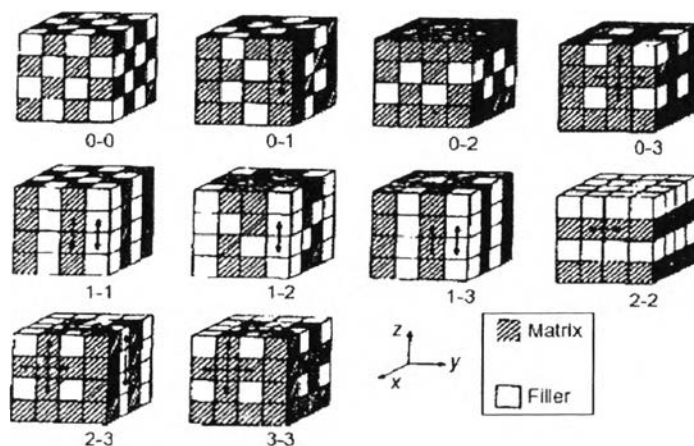

Figure 2.11 Connectivity patterns in a diphasic composite system (Lee *et al.*, 1989).

For high frequency applications, the composite materials which have high permittivity with low dielectric loss were produced. Recently, there are many research works that studied the dielectric behavior of 0-3 composite with different type of polymer matrix and ceramic filler.

Barium strontium titanates $Ba_{1-x}Sr_xTiO_3$ (BST) is a versatile ferroelectric compound for capacitors and high frequency devices due to its good electrical properties and low cost. (Tao *et al.*, 2007). Moreover, ferroelectric ceramic–polymer composites made of barium strontium titanate (BST) with different polymers, such as epoxy, polyvinylidene fluoride (PVDF), P(VDF-TrFE), silicone rubber, polyimide, polyvinylchloride, cyanoethylated cellulose polymer, polystyrene, and polyurethane etc., have been investigated because those polymers are low-cost materials with good thermal property, chemical stability, mechanical strength, and flexibility, and they can be easily processed even into complex shapes. In addition, some polymers have a very low loss tangent (Sonoda *et al.*, 2010). Nevertheless, there is no reported on the composite of the novel new phenolic resin, polybenzoxazine, and BST ceramics. Until in 2006 Panomsuwan G. investigated the polybenzoxazine-BST composite with 0-3 connectivity.

Generally, the percent loading volume and dispersion of the ceramic filler have influence to the dielectric properties of polymer-ceramic composite (Dias and Das-Gupta, 1996). The increasing of ceramic loading is used for obtain a high dielectric constant in composite, the amount of ceramic filler has to be more than 30 vol% but should not exceed 80 vol% because this is a suitable level that can change the permittivity of the composite and not reduce the processability of materials (Rao *et al.*, 2002). However, the incompatibilities between 2 materials still are a big common problem for preparation of polymer-ceramic composites. When these different materials are mixed, the ceramic particles tend to agglomerate and separate from the polymer matrix, as illustrated in Figure 2.12, resulting in an increase of dielectric loss of the material.
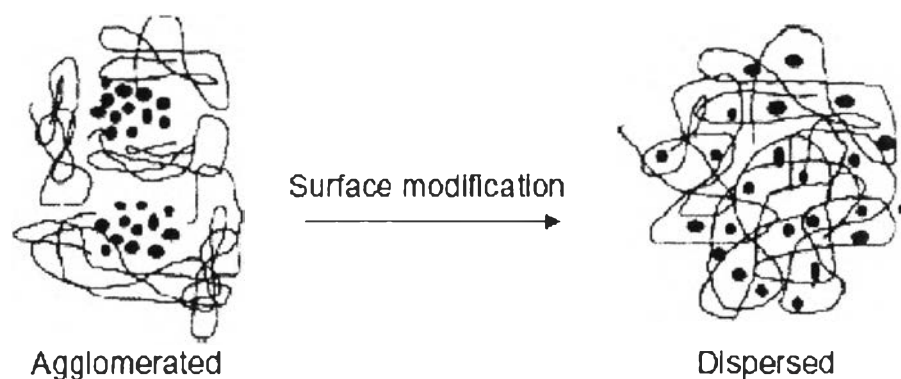
Agglomerated   Surface modification   Dispersed

Figure 2.12 Agglomeration and dispersion of ceramic particles into polymer matrix (Liang *et al.*, 1998).

One way to modify the compatibility of polymer-ceramic composite is the surface treatment of ceramic particles which improve the dispersion of ceramic fillers and make a higher dielectric constant of the composites. In this field, the silane coupling agent is used wildly, preferably via chemical bonds, for improve the dispersing and affect to dielectric properties of the composites. Silane coupling agents, which have two different functional groups, one that is attracted to the resin and the other that is attracted to the surface of the filler. That can provide an effective method to form good compatibility between ceramic fillers and polymer, because the not only absorb in a single layer on ceramic surface but also react with the polymer to form an interphase layer between them. When the good dispersion is occurred the dielectric constant of the composites will increase. (Dang *et al.*, 2006) the surface modification of ceramic particles with silane coupline agents is illustrated in Figure 2.13.
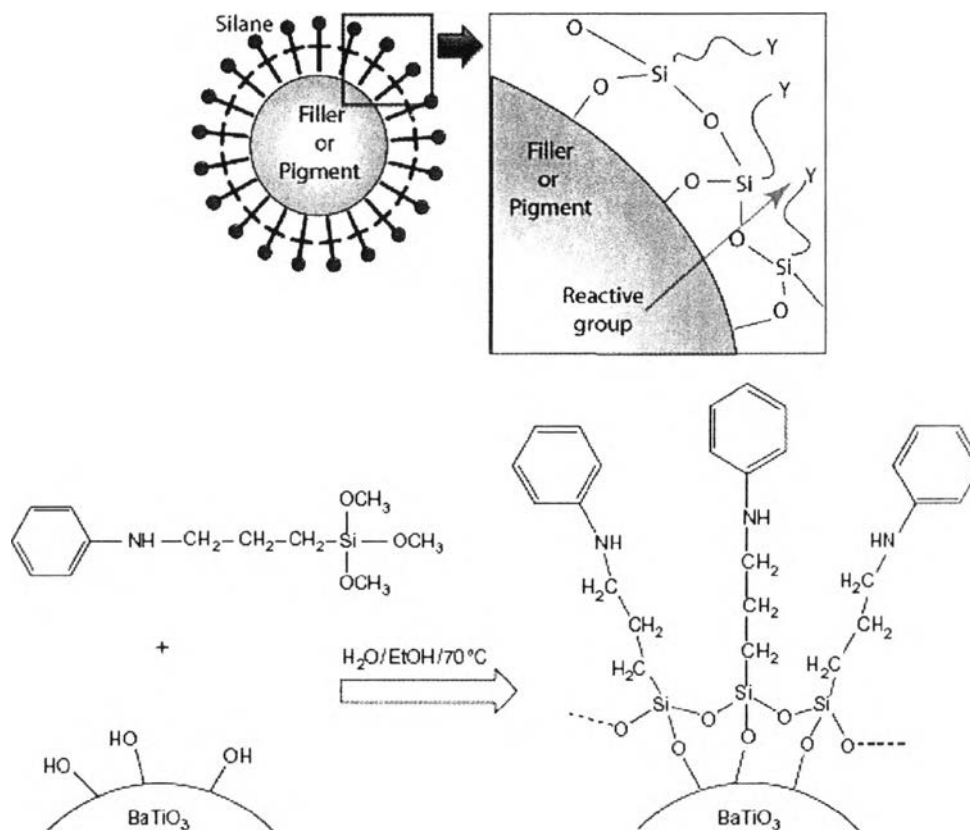
Figure 2.13 Surface treatment of BaTiO₃ with N-phenylaminopropyltrimethoxy silane (Liang *et al.*, 1998).

In 2006, Dang *et al.* studied the influence of a silane coupline agent on the morphology and dielectric propertied in BaTiO₃/polyvinylidene fluoride composite. γ-aminopropyltriethoxy-silane (KH550) was used as the coupling agent. The powders of BaTiO₃ were chemical modified with KH550 at concentrations of 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0 wt% of BaTiO₃ before dispersing into PVDF. Then the composite of BaTiO₃ with 40 wt% and PVDF was obtained. The results from SEM showed that the composites with BaTiO₃ modified by 1.0 wt% KH550 displayed a good dispersion of BaTiO₃ without any agglomeration. However, the dispersion and compatibility of composite are poor when the BaTiO₃ is not modified with KH550 or modified by more than 1.0 wt%, which show many pores and polymer aggregation. From IR spectra, they suggested that KH550 can act as bridge-liked action to bind the BaTiO₃ with PVDF, as shown in Figure2.14.
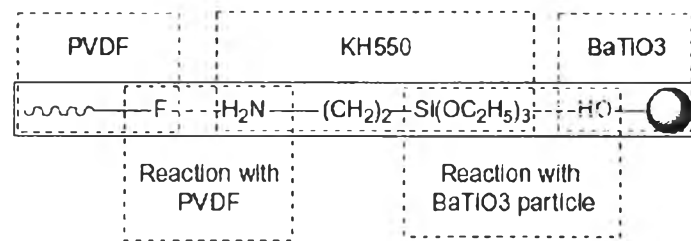
Figure 2.14 Chemical reaction process of γ- APS with both surface of BaTiO₃ and PVDF (Dang *et al.*, 2006).

From the dielectric measurement, they proved that dielectric constants of the composites with $BaTiO_3$ treated by less or more 1.0 wt% KH550 are almost the same as that of the composite with raw $BaTiO_3$. On the other hand, the dielectric constant of the composite with $BaTiO_3$ modified by 1.0 wt% KH550 can be improved about 20 % in comparison to the composite with raw $BaTiO_3$ without KH550 at a frequency from 10^3 to 10^5 Hz. Moreover, they also found that the dielectric loss of the composite with KH550 is less than 0.05 below 10^5 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 function 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 2.15. The central atoms can carry addition 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 delocalixation within the metal-Pc molecules.
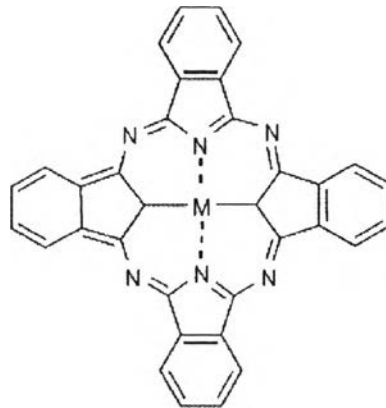
Figure 2.15 Structure of phthalocyanine (Pc) (Li Li *et al.*, 2005).

Li Li *et al.* (2005) tried to improve the dielectric property of epoxy- $BaTiO_3$ composite for embedded capacitor application by treating the surface of $BaTiO_3$ with phthalocyanine. They believed that phthalocyanine might from with the barium and titanium ions (Ba-Pc and Ti-Pc) on the surrounding surface of $BaTiO_3$ particles. Then good dispersion of $BaTiO_3$ in matrix and high dielectric constant could be obtained. From the dielectric measurement, the dielectric constant of polyamide-Pc coated $BaTiO_3$ composite film increased dramatically as they expected. The composite showed a dielectric constant of 80 and dielectric loss of 0.03 at 1MHz with a $BaTiO_3$ loading ratio of 70 vol%, which was much higher than that of the composite derived from commercial $BaTiO_3$.

However, there are some articles reporting about coating benzozazine monomer, as shown in Figure 2.16, 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.
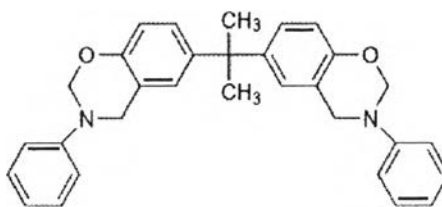
Figure 2.16 Benzoxazine monomer (Agag *et al.*, 2004)

According to thesis work of Kureson N. in 2008, she studied the dielectric properties of polybenzoxazine-unmodified BST powders composite with 30, 50, 80 wt% and with modified BST powders by using 3-aminopropyl trimethoxy silane, pthalocyanine and benzoxazine monomer are syrface modifiers with 30, 50, 80 wt%. Her result found that at the same frequency, the dielectric constants of the composites increased with the volume fraction of the BST ceramic powders. At higher ceramic filler loading volumes, the ceramic particles come closer, leading to an increased dipole-dipole interaction and contributing to a higher dielectric constant.

However, the loss tangents of all composites are greater than pure polybenzoxazine and tend to increase at higher ceramic content. The increase in the loss tangent value was attributed to the formation of porosity in the specimens as shown in Figure 2.17.
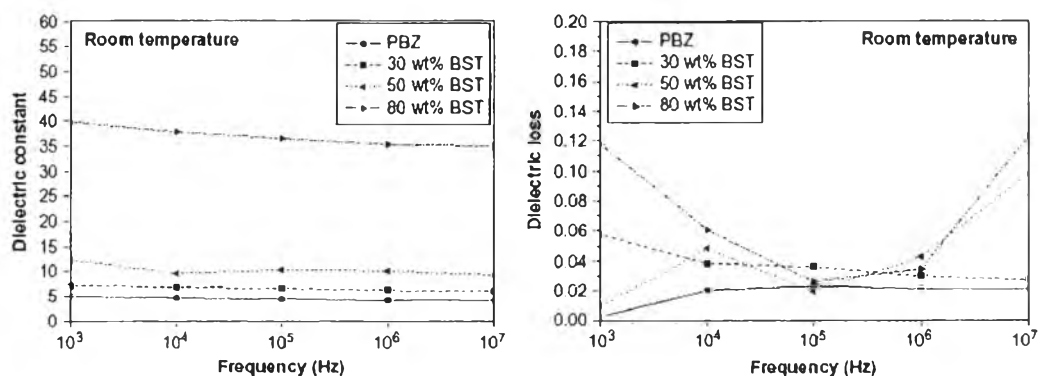

Figure 2.17 Frequency dependence of dielectric constant and dielectric loss for the composites at various BST contents (Krueson *et al.*, 2008).

As for the effects of surface modification on BST powders, it was observed that the modified BST surface could disperse better in a polybenzoxazine matrix compared with the unmodified BST powders. With regard to the dielectric properties, it was found that silane modification could improve the dielectric constant of the composites compared with the other methods because silane coupling agents can form chemical bonds on the surface of BST powders, the polarizability in the system could be enhanced, resulting in an increase in the dielectric constant. However, the composites with benzoxazine monomer and phthalocyanine-treated BST powders showed lower dielectric loss because this modification could prevent the BST agglomeration in the polymer matrix more effectively than the silane coupling modification (Krueson *et al.*, 2008).

According to the suitable dielectric properties of microwave application materials, the dielectric constant should be as high as possible and on the other hand, the loss tangent should be as low as possible. So, the effect of molecular structure on dielectric properties of aniline based and fluorine based polybenzoxaxine are studied. Moreover, the effect of surface modification on dielectric properties of polybenzoxazine-BST composites by using the silane compound, phthalocyanine and benzoxazine monomer are studied at high frequencies (microwave frequencies) too.

2.4 Dielectric Properties

2.4.1 Dielectric Properties in Solid Materials

The dielectric constant of materials is strongly influenced by polarization of the molecules, as shown in the Clausius-Mossotti relationship:

$$\frac{\varepsilon-1}{\varepsilon+2}\frac{M_w}{\rho} = \frac{N_A \alpha}{3\varepsilon_0} \tag{1}$$

where ε is the dielectric constant and α is the 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 that contribute to the total polarlization.

a.) Electronic polarization (α_e): an electric field will cause a slight displacement of the electrons of any atom with respect to the positive nucleus. As 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 (α_a): it 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 (α_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 and then it becomes less significant than the electronic mode.

Thus Equation (1) becomes equation (2) as follows:

$$\frac{\varepsilon-1}{\varepsilon+2}\frac{M_w}{\rho} = \frac{N_A(\alpha_e+\alpha_a+\alpha_o)}{3\varepsilon_0} \tag{2}$$

From equation (2), it can be observed that the dielectric constant will always scale with the polarlizability. The greater the sum of the three modes of polarization, the greater will be the dielectric constant. 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 (3)

$$\varepsilon = n^2 \tag{3}$$

where n is the refractive index referring to optical frequencies. Then substitution of equation (3) into equation (2) gives a quantity called the molar refraction of the material:

$$\frac{n^2-1}{n^2+2}\frac{M_w}{\rho} = \frac{N_A(\alpha_e+\alpha_a+\alpha_o)}{3\varepsilon_0}\qquad(4)$$

Equation (4) is 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 that are present will inevitably lag behind the applied field, giving rise to energy dissipation (such an effect is called dielectric relaxation). Mathematically, this is expressed as a phase lag d in the electric displacement:

$$D = D_0\cos(\omega t - \delta)\qquad(5)$$

which may be written as

$$D = D_1\cos\omega t + D_2\sin\omega t\qquad(6)$$

where $D_1 = D_0\cos\delta$ and $D_2 = D_0\sin\delta$

And an alternating electric field E, amplitude E_0, and angular frequency ω is

$$E = E_0\cos\omega t\qquad(7)$$

This leads to the defining of two relative permittivities

$$\varepsilon' = \frac{D_1}{\varepsilon_0 E_0}\quad\text{and}\quad\varepsilon'' = \frac{D_2}{\varepsilon_0 E_0}\qquad(8)$$

The loss tangent can then be defined as

$$\frac{\varepsilon'}{\varepsilon} = \tan\delta\qquad(9)$$

ε'' is called the dielectric loss factor and $\tan\delta$ is usually called the dielectric loss tangent. Alternatively, the 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).

2.4.2 Dielectric Properties of Polymer-Ceramic Composites

Composite material made of a ceramic and a polymer combines the superior properties of both polymer and ceramic, which results in a far better performance than that of the constituent materials. The ceramics possess a high dielectric constant with poor mechanical properties (brittleness), exhibit low dielectric breakdown strength, and require a high temperature process. On the other hand, polymers are flexible, easy to process at low temperatures, and possess a high dielectric breakdown field. By the combination of these two, composite materials with a high dielectric constant, good mechanical properties, ease of processing, and a high breakdown field to achieve high volume efficiency and energy storage density for applications of capacitors, electric energy storage devices, and transducers can be developed. The design of composites with optimum properties becomes a very great challenge as the electro active properties depend not only on the materials and the compositions, but also on their interconnections.

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 2.11 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 directions 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 common 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.

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 a higher dielectric constant. Rao et al. found that surface treatment of the ceramic using diblock copolymer surfactant helps to achieve a high dielectric constant of the composites at low ceramic loading by improving ceramic dispersion, which is better than a monomer surfactant.

With a view 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 most of the theoretical models fail when it comes to the 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). Various dielectric mixing models including the Yamada model, the Litchnecker model, the Bruggemann formulae, the modified Kerner expression can be fitted with the experimental results in order to select the model that will fit well with the experimental results and confirm the 0-3 connectivity of the ceramic filler in a composite type.

Many theoretical models have been proposed and used for predicting the dielectric constant of 0-3 connectivity composites in comparison with the experimental results. Widely used models include the Yamada model , Lichtenecker model, Bruggeman model and Kerner expression modified by Jayasundere-Smith (J-S prediction). The equations of these models are described as follows:

Yamada model $$\varepsilon = \varepsilon_p\left[\frac{\eta\phi(\varepsilon_c-\varepsilon_p)}{\eta\varepsilon_p+(\varepsilon_c-\varepsilon_p)(1+\phi)}\right]$$ (10)

Lichtenecker model $$\log\varepsilon = \log\varepsilon_p + \phi\log\left(\frac{\varepsilon_c}{\varepsilon}\right)$$ (11)

Bruggeman formulae $$\frac{\varepsilon_c-\varepsilon}{\varepsilon_c-\varepsilon_p}\left(\frac{\varepsilon_p}{\varepsilon}\right)^{1/3} = 1-\phi$$ (12)

Kerner expression $$\varepsilon = \frac{\varepsilon_p\phi_p+\varepsilon_c\phi_c[3\varepsilon_p/(\varepsilon_c+2\varepsilon_p)][1+3\phi_c(\varepsilon_c-\varepsilon_p)/(\varepsilon_c+2\varepsilon_p)]}{\phi_p+\phi_p(3\varepsilon_c)/(\varepsilon_p+2\varepsilon_c)[1+3\phi_c(\varepsilon_c-\varepsilon_p)/(\varepsilon_c+2\varepsilon_p)]}$$ (13)

where ε is the dielectric constant of the composites; ε_p and ε_c refer to the dielectric constants of the polymer matrix and the BST ceramic, respectively; ϕ_c is the volume fraction of the ceramic; and η is a shape parameter (Manuspiya et al., 2011).

2.4.3 Microwave Dielectric Properties of Polymer-Ceramic Composites

Microwaves are electromagnetic waves with wavelengths ranging from as long as one meter to as short as one millimeter, or equivalently, with frequencies between 300 MHz (0.3 GHz) and 300 GHz. This broad definition includes both UHF and EHF (millimeter waves), and various sources use different boundaries. In all cases, microwave includes the entire SHF band (3 to 30 GHz, or 10 to 1 cm) at minimum, with RF engineering often putting the lower boundary at 1 GHz (30 cm), and the upper around 100 GHz (3mm). Recently, the microwave frequency has very useful for electronic-telecommunication application such as mobile phone, wireless, microwave substrate and embedded device etc.

Development of electronic devices working at high operating frequencies, such as fast computers, cellular phones, etc., require new high-dielectric constant (high-K) materials that combine good dielectric properties with both mechanical strength and ease of processing. In particular, the high-K materials are required for making embedded capacitors for integrated electronic devices. The unique combination of dielectric and mechanical properties is hard to achieve in a one component material. Pure polymers are easy to process into mechanically robust

components but generally suffer from a low dielectric constant. On the other hand, typical high-K materials, such as ferroelectric ceramics, are brittle and require high-temperature processing, which is often not compatible with current circuits integration technologies.

Table 2.1 Summary of the microwave frequency application

Application	Frequency range
Mobile Broadband Wireless Access such as IEEE 802.20	1.6 - 2.3 GHz
Mobile phone networks, like GSM	1.8 - 1.9 GHz
WiMAX (Worldwide Interoperability for Microwave Access) based in the IEEE 802.16 specification	2 - 11 GHz
Wireless Internet for licensed long-range (up to about 25 km)	3.5 – 4.0 GHz
Bluetooth and the IEEE 802.11	2.4 GHz
ISM band	~ 5 GHz

Development of the composite materials for high frequency applications requires thorough understanding of the materials behavior at the frequencies of interest. However, only limited data are available in the literature for ferroelectric ceramic/polymer composites at the frequencies above 1 MHz, because of experimental difficulties related to high-frequency measurements. Nowadays, the systematic on the dielectric properties of ferroelectric ceramic/polymer composites over a broad frequency range including the microwave frequencies has been studied more (Popielarz *et al.*,2001) The barium titanate ($BaTiO_3$) which have high dielectric constant usually is used as a ferroelectric ceramic while the polymer matrixes were different. The matrixes include many polymeric materials such as epoxy resin, polyimide, rubber, polyacrylic acid, alkyd resin, polypropylene, and polyvinylidene fluoride, *et al.* In which, polyimide and epoxy resins were most suitable for electronic devices for good thermal endurance, dielectric and adhesive properties. The cost of polyimide was expensive comparing with epoxy resin, and its dielectric constant was lower than epoxy that led to lower filling effect. Benzoxazine resin is a

thermoset resin in low cost level same as epoxy resin. Compared with the epoxy resin, benzoxazine resin had better contour machining property, better mechanical property, better dielectric property stability, better fire resistance property, and low cost. Benzoxazine resin had applied successfully to electronic devices in recent years.

In 1996, Nancy E. F. and coworker studied the effect on the permittivity of two different base materials that was investigated with two types of fillers. The fillers utilized were a low permittivity material, alumina, and a high permittivity compound, barium titanate. The base materials investigated were epoxy and silicon rubber. Their result was shown that the base material does not significantly affect the permittivity of the composite. The choice of base material does influence the loss tangent, with silicon rubber filled materials exhibiting an increasing loss tangent at higher filler levels, while the epoxy samples showed stable value.

In 2001, Popielarz et $al.$ studied the effect of different polymer matrices on the dielectric properties of the composites at frequencies from 100 Hz to 10 GHz and at temperatures from -140 to+150 °C. It has been found that for the same $BaTiO_3$ content, the dielectric constant of the composite strongly depends on the type of polymer. Polar polymers increase the 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 the loss tangent, particularly within the intermediate frequency in the megahertz to gigahertz range.

In 2006, Hanbing et $al.$ prepared the benzoxazine/$BaTiO_3$ composite by the method of mixing. Experimental results indicated that the particle size and the content of the $BaTiO_3$ were affected strongly to the dielectric properties of the composite. The dielectric constant and dissipation of the composite were increased as particle sizes of the $BaTiO_3$ powder were increased from 50 nanometers to 1.81 micrometers. Moreover, the relation of the dielectric constant between the composite and the components was accorded with Lichtenecker logarithmic law in mixing. Effective dielectric constant of the $BaTiO_3$ in the benzoxazine resin matrix was 283, lower than its intrinsic dielectric constant. A composite was prepared and exhibited the high dielectric constant (ε_r = 54) which useful for microelectronic device. Panomsuwan et $al.$, (2006) synthesized the nanoparticles of BST at various Ba:Sr

ratios to fabricate the novel polybenzoxazine/BST nanocomposite with 0-3 connectivity at various filler contents. In this work, sol-gel $BaTiO_3$ powders, sintered $BaTiO_3$ powders, and sol-gel $Ba_{0.7}Sr_{0.3}TiO_3$ powders, SG-BST, were used as the ceramic fillers, and polybenzoxazine was used as the polymer matrix. The ceramic powders were added to the benzoxazine monomer powder in amounts of 30, 40, 50, 60, 70, and 80 wt%. The dielectric measurement of the composites revealed that the dielectric constants of all composites are weakly dependent on frequency (100 Hz-10 MHz). The higher ceramic content leads to a higher composite dielectric constant. It also showed that the composite with 80 wt% of sol-gel $Ba_{0.7}Sr_{0.3}TiO_3$ powder provides the highest dielectric constant, 28 (at 1 kHz; tends to be lower at high frequency), which is greater than that of pure polybenzoxazine by around four times, and provides a 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 2.18 and Figure 2.19, respectively. As can be seen in Figure 2.19, it was found that the dielectric constant increased with higher ceramic content. The dipole-dipole interaction increased and contributed to a higher dielectric constant when ceramic fillers came closer at higher filler loading. For the composites with 80 wt% (48 vol %) of SG-BST, the composite had a dielectric constant as high as 28, at 1 kHz.
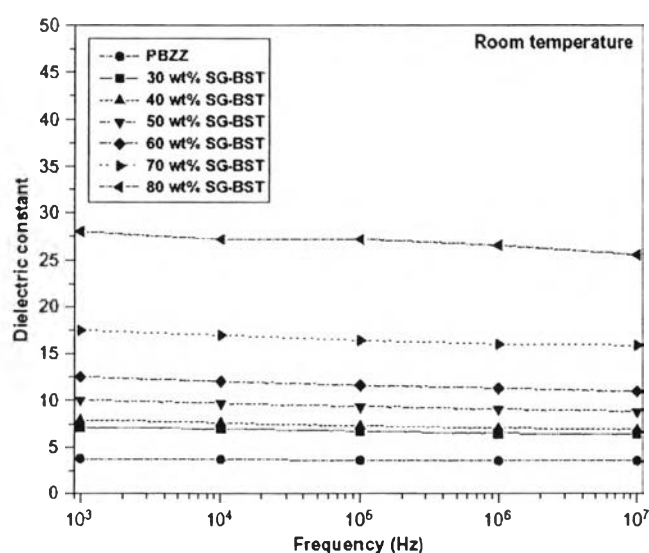

Figure 2.18 Frequency dependence of dielectric constant of the composite at various sol-gel BST contents (Panomsuwan *et al.*, 2006).
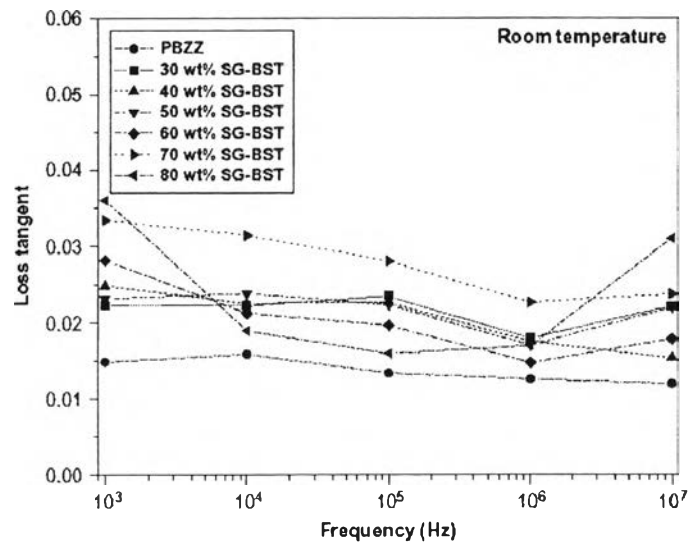
Figure 2.19 Frequency dependence of dielectric loss of the composite at various sol-gel BST contents (Panomsuwan *et al.*, 2006).

In 2007, Cheng *et al.* studied the dielectric constant of the epoxy with various weight percent of $BaTiO_3$ in microwave frequency. It was found that by adding the ceramic powder, the dielectric constant of the composite increases which the dielectric constant could be increased from 3.2 of the sample without fillers to 13.1 of the epoxy containing 80 wt% of $BaTiO_3$ at 1 GHz. And the Lichtenecker's mixing model can fit the measured data very well. It was found that, at the lower frequency, the permittivity decreases with increasing frequency, but after about 100 MHz the changes can be ignored.