CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Toughening of Benzoxazine-Based Formulations

Among phenolic resins, the group of benzoxazines is outstanding and pays an important role in academia and industry. The molecular design flexibility of benzoxazines certain desired properties can be tailored leading to potentially open up new applications and product opportunities with comparative low cost of starting materials for synthesis. Particularly, the following characteristics such as room temperature storage ability, self-polymerization behavior (allows heat curing one component formulations), excellent FST (fire, smoke, toxicity) properties, low cure shrinkage, low cure heat release, viscosity adjustable for product forms and application needs, good thermal stability and durability, low moisture absorption, low water uptake, high glass transition temperatures (T_{gs}), excellent retention of hot/wet properties, high compression strength and modulus, as well as possibility of copolymerizations with other resins attribute to the high attentiveness in this material type from an industrial point of view (Sawaryn, et al., 2011).

However, many cross-linked benzoxazine-based systems derived from monomeric precursors face the major drawback of brittle materials that can easily break. As a result, the benzoxazine-based systems require the effective approaches to improve the toughness so as to potentially extend new applications.

2.1.1 Poly(benzoxazine/urethane) Alloys

The alloying is a versatile method to enhance the toughness of polybenzoxazine by simply mixing with available flexible polymers. By blending with ones such as urethane elastomer (Takeichi, et al., 2000), epoxy (Rimdusit, et al., 2005), poly (ε-caprolactone) (Ishida, et al., 2001), and polydimetylsiloxane (Ardhyananta, et al., 2009) can improve toughness and extend processing capability. Among these resins, combining with urethane is interesting and easy to carry out.

Polyurethane (PU) elastomers are one of the valuable engineering materials with the essential distinctive criterion, which are composed of the soft segments derived from polyols and hard segment from isocyanates and chain extenders. Polyurethanes offer the prominent properties in terms of good abrasion resistance, outstanding oil resistance, excellent low-temperature flexi-bility, and extraordinary processibility. For these above potentials of PUs provide the materials with improving the characteristics of either high modulus or good elasticity. Nonetheless, polyurethane elastomers have some disadvantages such as low resistance to moisture and hydrolysis, low resistance to polar solvents, and poor thermal stability. (Petrovix, Z.S., and Ferguson, J., 1991). Thus alloying materials made of polybenzoxazines and polyurethane are a good alternative to get rid of the drawbacks of both components and combine the superior properties of them, which results in a far better performance than that of the constituent materials. Recently, there are a numerous scientists that reported polybenzoxzaine/polyurethane alloyed as follows:

Takeichi and coworkers (2000) have successfully developed clear poly(urethane-benzoxazine) films as novel polyurethane (PU)/phenolic resin composites based on BA-a resin and toluene diisocyanate (TDI)/polyethylene adipate polyol-typed urethane resin as shown in Figure 2.1 All the films obtained showed only single glass transition temperature (T_g) from viscoelastic measurements, indicating no phase separation in poly(urethane-benzoxazine) due to the in situ polymerization. The T_g increased with the increasing of Ba content. The films containing less than 15% of Ba offered characteristics of an elastomer. These elastic films exhibited good resilience with excellent reinstating behavior. The films containing more than 20% of Ba had characteristics of plastics. The poly(urethane-benzoxazine) films showed excellent resistance to the solvents and thermal stability of PU by the incorporation of a small amount of Ba.
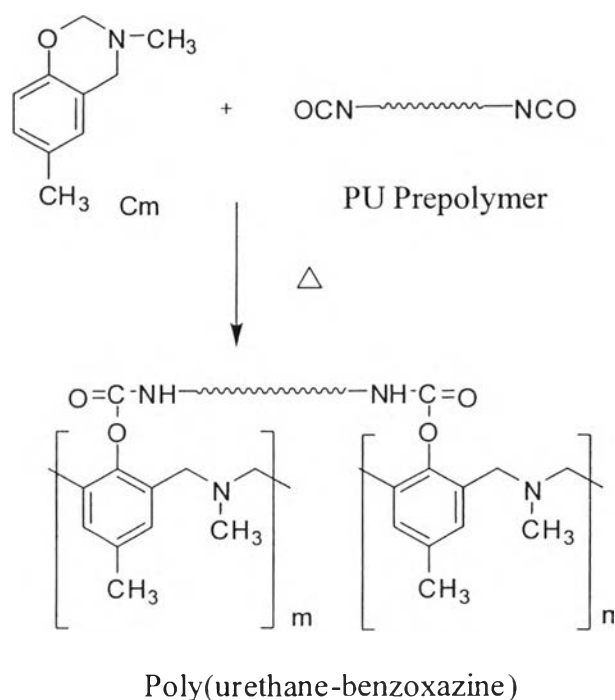
Poly(urethane-benzoxazine)

Figure 2.1 Reaction 3,4-dihydro-3.6-dimethyl-2H-1,3-benzoxazine,Cm-type polybenzoxazine and PU Prepolymer. (Takeichi *et al.* 2000)

Rimdusit *et al.* (2005) improved the toughness of aniline-based (BA) polybenzoxazine by alloying with isophorone diisocyanate (IPDI)-based urethane pre-polymers (PU) and with flexible epoxy (EPO732). The polybenzoxazine/polyurethane alloyed showed greater improvement in flexural, toughness and thermal stability properties than poly(BA-a)/EPO732 component. Alloying with highly flexible molecular components shifted the curing temperature of the benzoxazine resin to a higher value. Interestingly, the enhancement in the glass transition temperature (T_g) of BA-a/PU alloys was clearly observed, i.e., T_g of the BA-a/PU alloys were significantly higher (T_g beyond 200 °C) than those of the parent resins, i.e., 165 °C for BA-a and −70 °C for PU. However, this characteristic was not observed in the BA-a/EPO732 alloy systems. The enhanced T_g of the BA-a/PU alloyed at a 70/30 mass ratio was found to be 220 °C, while that of BA-a/EPO732 at the same mass ratio was observed to be only 95 °C. The char yield of both alloy systems was steadily enhanced with the increased benzoxazine content

because the char yield of the polybenzoxazine was inherently higher than that of the two tougheners. The structure of three components was shown in Figure 2.2
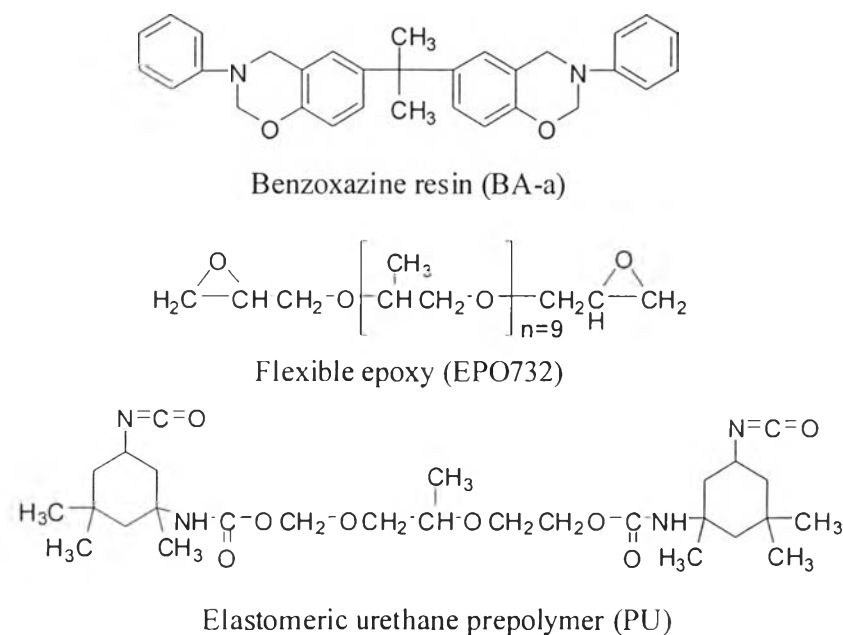

Benzoxazine resin (BA-a)

Flexible epoxy (EPO732)

Elastomeric urethane prepolymer (PU)

Figure 2.2 Chemical structure of three resins used. (Rimdusit *et al.* 2005)

In 2008, Rimdusit and coworkers studied the effect of polyol molecular weight (Using various Mn of the poly (propylene glycol) i.e., 1000, 2000, 3000, and 5000 g/mol) on properties of benzoxazine-urethane polymer alloys. The flexural strength of the BA:PU alloys exhibited a synergistic behavior with the ultimate value at BA:PU = 90:10 for every molecular weight of the polyol used. When 30% of polyurethane was introduced in the system, the flexural modulus of polybenzoxazine would be decline. The char yield increased when the higher molecular weight of polyol had added. Then, thermomechanical characteristics of benzoxazine-urethane copolymers and their carbon fiber-reinforced composites were investigated. For this research area, toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) was used to substitute the isophorone diisocyanate (IPDI). The effect of urethane prepolymer based on TDI rendered the highest T_g, flexural modulus, and flexural strength of the copolymers among the three isocyanates used.

High processable carbon fiber composites were based on TDI at which 80 wt.% of the fiber in crossply orientation provided relatively high valued of about 490 MPa.

Jamshidi *et al.*, (2010) developed a new method for the combination of polyurethanes (PUs) and polybenzoxazine (PBZ) to attain novel thermoset poly(urethane-co-benzoxazine)s with good thermal, mechanical, and electrical properties as well as low temperature curing profile. The preparation route of poly(urethane-polybenzoxazine) networks was shown in Figure 2.3. The key of this work was to take advantage of the fact that phenolic compounds with free ortho or para positions act as initiators for ring-opening polymerization of benzoxazine compounds, and an aminoalkylation reaction occurred preferentially at the ortho and para positions of phenols. Firstly, NCO terminated urethane prepolymers were prepared from the reaction of poly(tetramethyleneether glycol), and 2,4-tolylene diisocyanate, and then end functionalized with bisphenol-A under proper condition. DSC, DMTA, and gel content measurements were applied to find optimum ring opening polymerization condition (170 °C for 1 h. and 200 °C for 15 min.). Various kinds of thermoset polymers were prepared by the reaction of PTPU at different molecular weights with variable contents of Ba. The results showed that overall flexibility increased with increase in PTPU molecular weight and decrease in Ba content. PU3Ba30 and PU3Ba samples showed elastic properties at ambient condition. The thermal stability of networks was improved by increasing PTPU molecular weight as well as Ba content. PU3Ba70 showed the highest thermal stability between studied formulations.
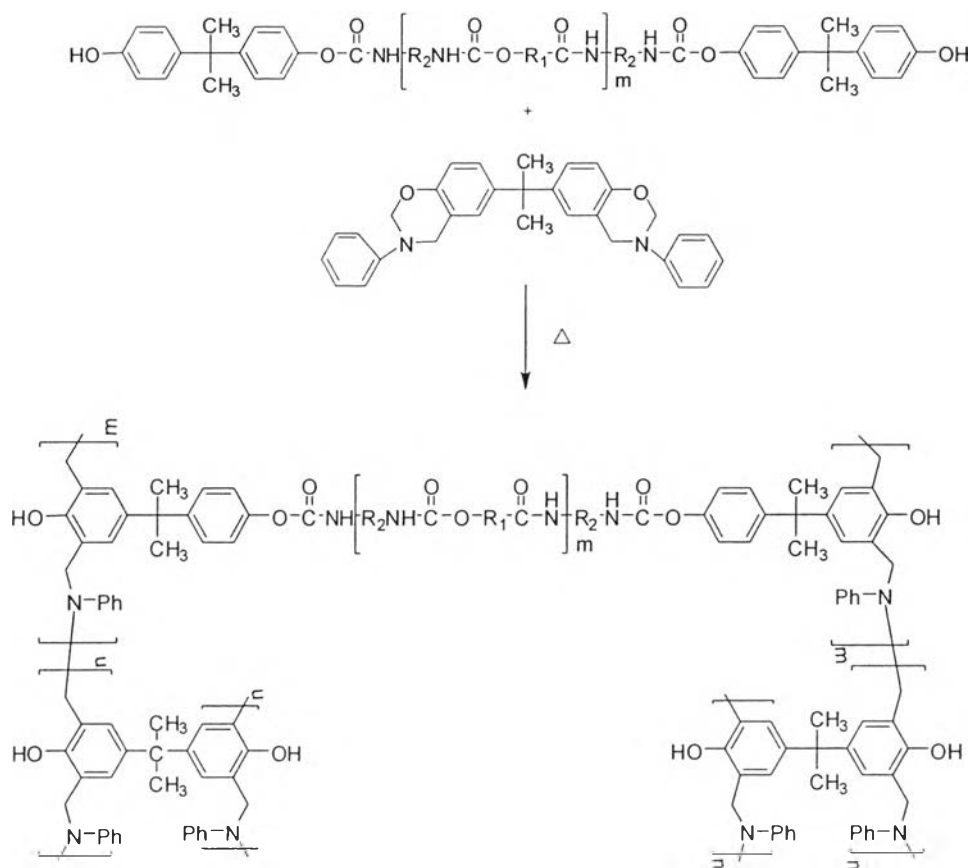
Figure 2.3 Preparation poly(urethane-benzoxazine) networks. (Jamshidi *et al.*, 2010)

In the same year, Jamshidi and coworkers conducted the combination between polyurethanes and polybenzoxazines. For this purpose, p-nitrophenol blocked polyurethanes (BPUs) were prepared via the reaction of poly(tetramethylene ether) glycol of various molecular weights, 2,4-tolylene diisocyanate and p-nitrophenol. The BPUs were then mixed with 2,2-bis(3,4-dihydro-3-phenyl- 2H-1,3-benzoxazine) propane (Ba) at various weight ratios. Both of reports led to the conclusion that the increasing the Ba content or decreasing the PTPU molecular weight resulting in reaching the maximum dielectric strength, minimum dissipation factor and the electrical properties were improved much better when increased Ba. Dissipation factor indicated the tendency of a material to convert electrical energy to heat. Dielectric constant indicated the ability of an insulator to store electrical energy. The synthesis route of PU and preparation of poly(urethane-benzoxazine) networks were shown in Figure 2.4 and 2.5.

$$R_1 = -CH_2CH_2CH_2CH_2O \left(CH_2CH_2CH_2CH_2O \right)_n CH_2CH_2CH_2CH_2-$$

$$R_2 = \text{—}\underset{}{\bigcirc}\text{—}CH_3$$

$$n \ HO\text{-}R_1\text{-}OH \quad + \quad 2n \ OCN\text{-}R_2\text{-}NCO$$

$$n \ OCN \left[R_2\text{—}NH\text{—}\overset{O}{\underset{}{C}}\text{-}O\text{-}R_1\text{-}O\text{-}\overset{O}{\underset{}{C}}\text{—}NH \right]_m R_2\text{-}NCO$$

ITP1-1

$$2n \ HO\text{—}\bigcirc\text{—}NO_2$$

$$O_2N\text{—}\bigcirc\text{—}O\text{-}\overset{O}{\underset{}{C}}\text{-}HN \left[R_2\text{-}HN\text{-}\overset{O}{\underset{}{C}}\text{-}O\text{-}R_1\text{-}O\text{-}\overset{O}{\underset{}{C}}\text{-}NH\text{-}R_2NH\text{-}\overset{O}{\underset{}{C}}\text{-}O \right]_m \bigcirc\text{—}NO_2$$

BPU1-3

Figure 2.4 Synthesis route for the preparation of BPUs. (Jamshidi *et al.*, 2010)

BPU1-3   +   Ba

X : H or —CONH~~PU~~

Figure 2.5 Preparation of poly(urethane-benzoxazine) networks. (Jamshidi *et al.*, 2010)

Baqar *et al.* (2011) proposed a novel concept that has been developed to produce phenolic resin/polyurethane copolymers via benzoxazine chemistry as displayed in Figure 2.6. Through one-pot synthesis, a series of linear poly(benzoxazine-co-urethane) materials has been synthesized via the reaction of a newly developed dimethylol functional benzoxazine monomer with 4,4'-methylene diphenyl diisocya-nate and poly(1,4-butyleneadipate). For the promising of this work, one-pot synthesis of phenolic-urethane materials cloud avoid the shortcomings associated with the use of preformed NCO terminated PU prepolymers, exhibited superior thermal stability compared to previous methods and the well-known high performance poly(urethane-imide) excellent mechanical integrity as can be seen from high tensile modulus and tensile strength owing to the presence of polybenzoxazine as part of the main-chain.
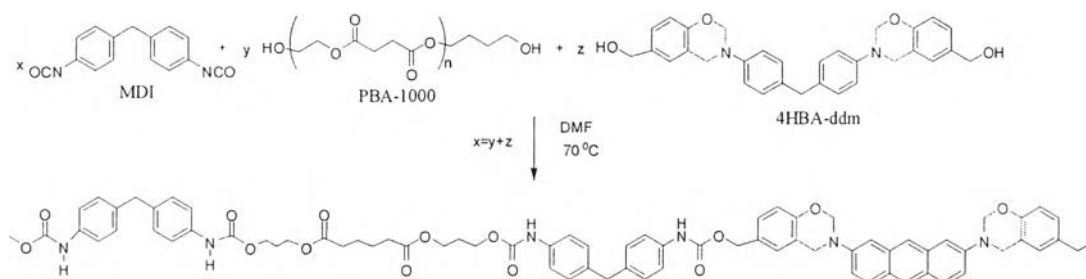

Figure 2.6 Preparation of main-chain poly(benzoxazine-co-urethane)s. (Baqar *et al.* 2011)

Rimdusit and coworker (2011) studied properties of benzoxazine-urethane copolymer with varying compositions. This study was found that the increasing PU fraction significantly enhanced crosslink density of the obtaining polymer alloy. The BA-a fraction affected the amount of char yield and water absorption. At the Ba-a/PU =90/10 mass ratio showed the minimum CTE and maximum in flexural strength. The results revealed that a processing gap of the BA-a/PU mixtures was broadened with the increasing urethane prepolymer fraction, which the liquefying temperature was lowered and the gel point shifted to higher temperature with the amount of the PU. The combination of two components exhibited the single with higher glass transition than those parents.

2.1.2 High Molecular Weight Polybenzoxazine Precursors

Since the normal brittle nature of monomeric benzoxazines derived from the termination of the chain propagation by the intramolecular six-membered ring hydrogen bonding due to the chain ends (Laobuthee, *et al.*, 2001). To alleviate the creation of undesired chain end groups, the prominent class of polybenzoxazine precursors known as main-chain type benzoxazine polymers (MCBP), was suggested. The utilized MCBP method relates to the use of various diamines such as aromatic or aliphatic and bisphenols as starting materials of benzoxazine synthesis.

In 2005, Tsutomu and coworkers proposed the synthesis route of ethylenediamine (eda), and hexamethylenediamine (hda) and methylenedianiline (mda) based polybenzoxazine via solvent method as seen in Figure 2.7. All of precursors containing cyclic benzoxazine groups in the backbone showed considerably improved toughness than the typical polybenzoxazine, poly(BA-a), because of the long linear backbone and high crosslink density. This approach is shown to be effective in providing tough polybenzoxazines with high T_g and thermal stability. The T_g values of polybenzoxazines from the high molecular weight precursors were 238–260 °C, much higher than the T_g of the typical poly(BA-a) (171 °C). Thermal stability of the polybenzoxazine depended on the aromatic content, and polybenzoxazine from aromatic diamine (BA-mda) showed higher thermal stability and flexibility than that of PBA-a.
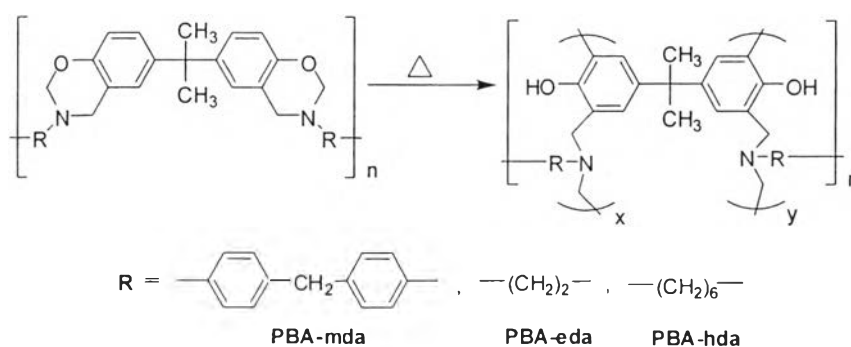

Figure 2.7 Tentative structures of high molecular weight polybenzoxazine precursors and the cure resin. (Tsutomu T. *et al.* 2005)

2.2 Barium Strontium Titanate (BST)

A common class of perovkite barium stronium titanate (BST, $Ba_{1-x}Sr_xTiO_3$), as shown in Figure 2.8 is derived from barium titanate ($BaTiO_3$), which exhibits good dielectric properties and has been extensively used in high dielectric capacitors. It is known that ceramics will show the highest dielectric constant at Curie temperature, T_c (the temperature at which the ceramics show a ferroelectric-paraelectric phase transition (Tetragonal-cubic), as seen in Figure 2.9. 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 by adding a variety of isovalents (e.g. Sr^{2+}, Pb^{2+}, etc.). It was found that the substitution of strontium for barium to form barium strontium titanate (BST, $Ba_{1-x}Sr_xTiO_3$) is potential approach to decrease the Curie temperature lineraly. In addition, for a barium-rich composition (x<0.35), BST is ferroelectric at room temperature. As strontium molar fraction increases, the Curie temperature of BST shifts to lower room temperature. Thus BST can be a paraelectric at room temperature to perfrorm a high dielectric constant, low tangent loss, and large dielectric breakdown strength (Lu *et al.*,2003). Furthermore, Ioachim and coworker found that the increasing inconcentration of Sr had 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)
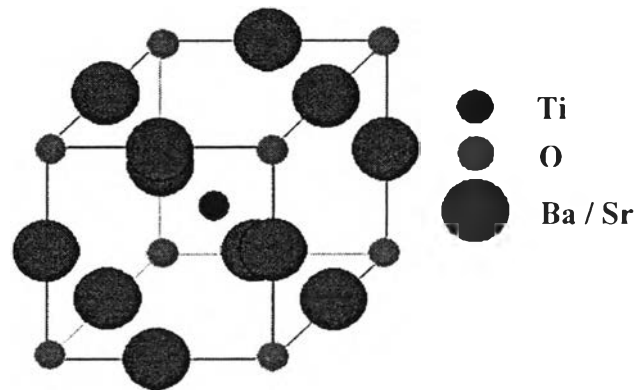
Figure 2.8 Unit cell of Perovkite barium stronium titanate (BST, $Ba_{1-x}Sr_xTiO_3$). (http://www.doitpoms.ac.uk/tlplib/ferroelectrics/printall.php).

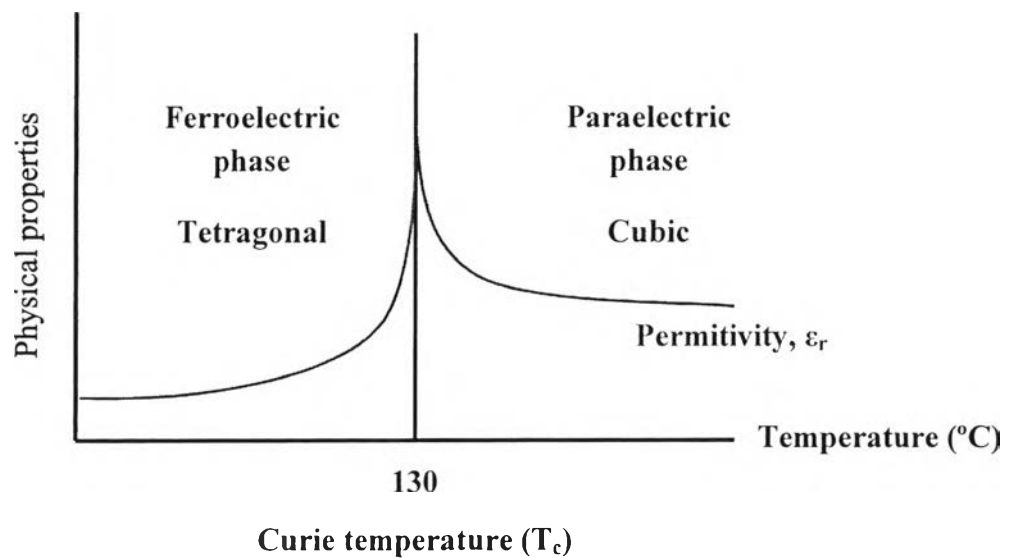**Figure 2.9** Phase transition in Perovkite barium stronium titanate (BST, $Ba_{1-x}Sr_xTiO_3$).

      For various works, sol-gel method operated at lower temperature process was extensively performed in order to prepare BST powders because this process offers considerable advantages which are useful and possible to obtain high purity and homogeneity materials (shaped as monolithic blocks, powders or thin layers). These approaches provide 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.*,2002).

Hu *et al.*, (2004) prepared ceramic powders ($Ba_{0.7}Sr_{0.3}TiO_3$) via sol-gel method. The operation at 800 °C for 2 h of calcination process obtained the powder sizes around 50-100 nm, which were smaller than particle prepared from conventional solid state reaction. Furthermore, their sintering temperature at 1250 °C was lower as well.

Panomsuwan *et al.*, (2006) synthesized the BST powder nano-size by using the sol-gel method with a variety of the strontium molar fractions (x); x = 0, 0.3, 0.5 and 0.7 in order to adjust the Curie temperature and obtain BST ceramic in paraelectric and ferroelectric phase at room temperature. The effects of the concentration of strontium on the microstructure and the dielecric properties of this ceamic were studied as well. From experimental data, the result showed that the shape and size distribution of BST particles were uniformity in which an average diameter were around 50 nm. Moreover, the structure of sol-gel BST ceramics at x=0 and 0.3 after sintering process changes to tetragonal structure while ceramics with x=0.5 and 0.7 still exhibited the same as cubic structure and the uniformity of grain sizes would be obtained at 1400°C of sintering temperature for all of BST compositions. The maximun of dielectric constant (~2700) was received at 0.3 mole fraction of strontium when measured BST ceramics at room temperature. However, above 1 MHz, the dielctric constant would drop rapidly. In contrast, the dielectric loss increased due to the dipolar relaxation. These observation cloud indicate that dielectric properties significantly depend on frequency. Although the dielectric constant of BST ceramics with x = 0.5 and 0.7 is lower than those with x = 0 and 0.3, BST powders showed lower dielectric loss at high frequency as shown in Figure 2.10 and 2.11, respectively.

The suitable dielectric properties of microelectric device which used in high frequency should exhibit moderate to high in dielectric constant, and also low dielectric loss. Therefore, Krueson and Sapmaneenukul continued to develop the dielectric substrates from polybenzoxazine/BST composites by choosing 0.7 strontium mole fraction as BST ceramic fillers.
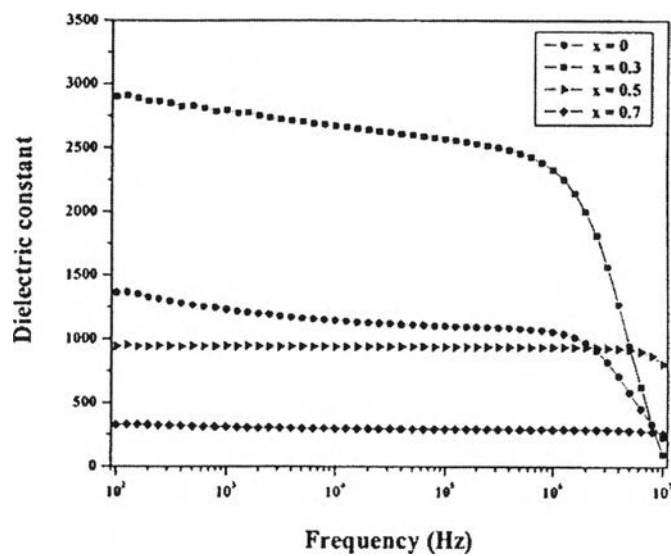
Figure 2.10 Dielectric constants of $Ba_{1-x}Sr_xTiO_3$ ceramics at room temperature.
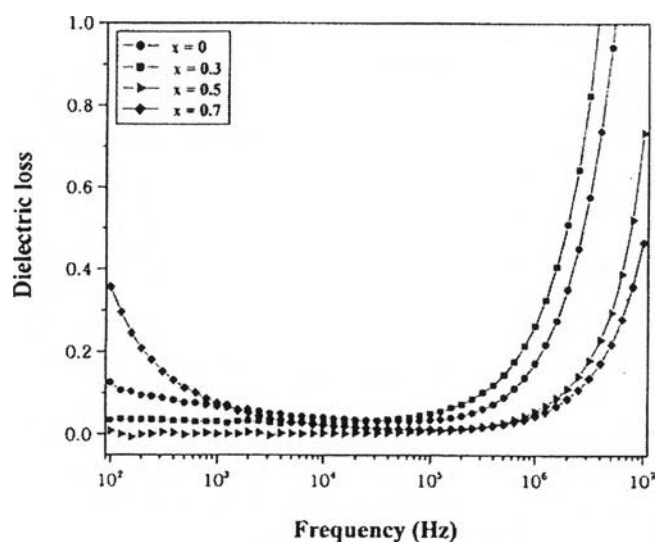(Panomsuwan *et al.*, 2006)

Figure 2.11 Dielectric losses of $Ba_{1-x}Sr_xTiO_3$ ceramics at room temperature.
(Panomsuwan *et al.*, 2006)

2.3 Polymer-Ceramic Composite

For producing dielectric materials with excellent properties at microwave frequency, it is well-know that one particular composition material cannot meet the desired properties. Thus the combination of different materials is expected to be an effective approach to fabricate composites with high quality, especially for polymer-matrix composites (PMC). The most common fillers are added in the matrix such as metals, ceramics, carbon based materials, and organic fillers such as semi-conductive oligomer and conducting polymers.

Nowadays, polymer-ceramic composites have been extensively selected as a major material candidate for the development of dielectric materials because they combine the superior properties and remedy the shortcomings of the two components. This combination produces the excellent performance beyond those of parent materials lending their usage to the applications in construction (Dang Z. *et al.*, 2012). Ceramics are mostly high stiffness, excellent thermal stability, and high dielectric constant. For shortcomings of them are high density, low dielectric breakdown strength, brittleness and challenging processing conditions, which impede their usage as high-k materials. While, the advantages of polymers are easy processing and mechanical flexibility and low cost (Ulrich RK *et al.*, 2003).

2.3.1 Connection Type of Polymer-Ceramic Composite

The use of dissimilar materials in the PMC originates interfaces which have significance on final properties. Since both of dielectric and mechanical properties are not only depend on the materials; matrix (continuous), and dispersed phase (particulates, fibers) but also on their interconnection; properties of phases, geometry of dispersed phase (particle size, distribution, orientation), and amount of phase (Bai *et al.*, 2000). This uniform concept is called connectivity and was first introduced by Newnham.

In general, there are 10 different patterns for binary composites on the basis of connectivity: 0–0, 0–1, 0–2, 0–3, 1–1, 1–2, 1–3, 2–2, 2–3, and 3–3, which are illustrated in Figure 2.12 (Dang *et al.*, 2012). Among the connectivity patterns often designed to fabricate filler/polymer-matrix composites, composites of 0–3

connectivity (a three-dimensionally connected polymer phase is loaded with isolated ceramic particles) are the most attractive from the application point of view. Since they allow an opportunity to manufacture materials combining the electrical and mechanical properties of both polymers and ceramics, the flexible forms and very various shapes with very inexpensive fabrication methods for mass production including simply mixing and molding can be feasible (Sebastian *et al.*, 2010).
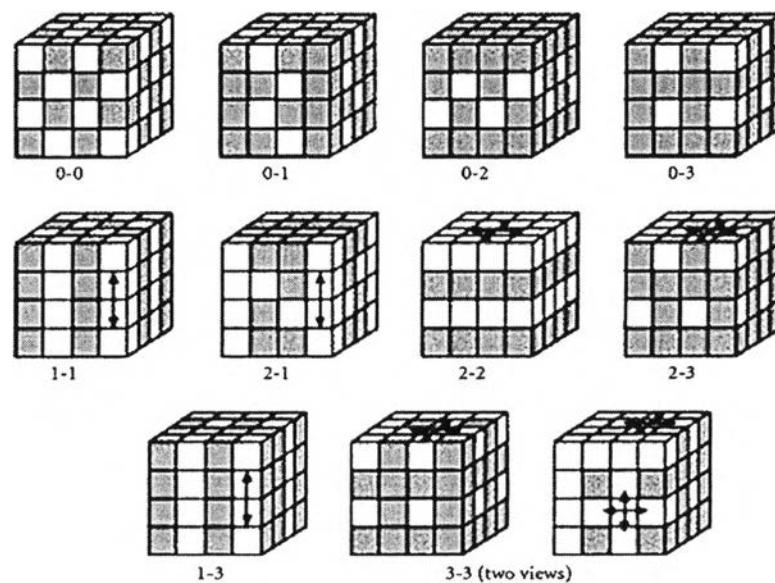

Figure 2.12 Ten connectivity patterns for two-phase composites. (Rashed Adnan Islam and Shashank Priya 2011)

For the previous work, diamine-based polybenzoxazine /BaTiO$_3$ composites with 0-3 connectivity as a new type of dielectric materials were reported by Panomsuwan and co-workers. The result revealed that this novel composite showed good dielectric characteristics in the frequency range of 1 kHz – 10 MHz . Later on, Krueson, *et al.* (2008) developed the material by introducing other kinds of polybenzoxazine (fluorine and amine based) combined with BST, which derived from doped barium titanate with strontium in order to shift Curie temperature to lower to obtain high dielectric constant at room temperature. This research displayed the improvement in dielectric properties of the composites.

Until now, Sapmaneenukul *et al.* (2012) reported the high dielectric constant and low loss tangent which determined at microwave frequency of the polybenzoxazine-BST composites. The result showed that aniline-based benzoxazine monomer exhibited the better dielectric properties than fluorine-based benzoxazine monomer.

Nevertheless, the incompatibility between 2 materials still is a major problem for polymer-ceramic composite preparation. When these dissimilar materials are mixed, the ceramic particles tend to agglomerate and separate from the polymer matrix, resulting in obtaining poor dielectric properties (Liang *et al.* 1998).

To improve the compatibility between polymer and ceramic, surface treatment on ceramic particles is an alternative way. In the past, the effective chemical agent for dispersing the ceramic particles was silane coupling agent. It consists of two different functional groups, one that is attracted to the resin and the other that is attracted to the surface of the filler. These evidences can provide an effective connection 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. The good dispersion leads to obtain the good dielectric characteristics of the composites. (Dang *et al.*, 2006). As another interesting method to diminish the agglomeration of ceramic fillers is by using polymer matrix as a surface modifier.

Krueson and Sapmaneenukul prepared the polybenzoxazine/BST composites by chemically treated $Ba_{0.3}Sr_{0.7}TiO_3$ powders with 3-aminopropyl trimethoxy silane, benzoxazine monomer, and phtalocyanine. It was found that silane treatment was more effective to improve dielectric properties (high dielectric constant with low dielectric loss) than other surface modifiers. Bulky group, benzoxazine and phtalocyanine, potentially prevented the ceramic agglomeration and slightly uplifted the dielectric properties; therefore, treatment by benzoxazine monomer was preferably in term of cost effective.

2.4 Dielectric Properties

2.4.1 Dielectric Properties in Solid Materials

Dielectric properties are composed of the non long-range conducting electrical characteristic of a material. Dielectric responses originate from the short-range motion of charge carrier under the influence of an applied electric filed. The motion of charges leads to the storage of electrical energy and the capacitance of the dielectric. Subsequently, as the beginning step in determining dielectric behaviors, the definition of capacitance should be considered.

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.

$$C = \frac{Q}{V} = \frac{Coulombs\ (C)}{Volt\ (V)} = Farad\ (F) \tag{1}$$

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 ε_0, the permittivity of free space, and is equal to 8.854×10^{-12} C^2/m^2 or F/m. Thus the capacitance of a parallel-plate capacitor will be equal to:

$$Q = qA = \pm \varepsilon_0 EA = \varepsilon_0 \left(\frac{V}{d}\right) A \tag{2}$$

$$C_0 = \frac{Q}{V} = \frac{\varepsilon_0\left(\frac{V}{d}\right)A}{V} = \frac{\varepsilon_0 A}{d} A \tag{3}$$

When a material is inserted between the plates the capacitance is increased.

$$C = \frac{A\varepsilon_0\varepsilon'}{d} A \tag{4}$$

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

$$\frac{\varepsilon'-1}{\varepsilon'+2}\frac{M_w}{\rho} = \frac{N_A\alpha}{3\varepsilon_0}$$ (5)

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 (5) becomes equation (6) as follows:

$$\frac{\varepsilon'-1}{\varepsilon'+2}\frac{M_w}{\rho} = \frac{N_A(\alpha_e+\alpha_a+\alpha_o)}{3\varepsilon_0}$$ (6)

From equation (6), 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 (7)

$$\varepsilon' = n^2 \tag{7}$$

where n is the refractive index referring to optical frequencies. Then substitution of equation (7) into equation (6) gives a quantity called the molar refraction of the material:

$$\frac{n^2-1}{n^2+2}\frac{M_w}{\rho} = \frac{N_A(\alpha_e+\alpha_a+\alpha_o)}{3\varepsilon_0} \tag{8}$$

Equation (8) 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:

$$D = D_0 \cos(\omega t - \delta) \tag{9}$$

which may be written as

$$D = D_1 \cos\omega t + D_2 \sin\omega t \tag{10}$$

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

$$E = E_0 \cos\omega t \tag{11}$$

This leads to the defining of two relative permittivities

$$\varepsilon' = \frac{D_1}{\varepsilon_0 E_0} \quad \text{and} \quad \varepsilon'' = \frac{D_2}{\varepsilon_0 E_0} \tag{12}$$

The loss tangent can then be defined as

$$\frac{\varepsilon''}{\varepsilon'} = tan\ \delta \tag{13}$$

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) (Manuspiya et al., 2011).

2.4.2 Dielectric Properties of Polymer-Ceramic Composites

The explanation and prediction of dielectric constant of the composites from the dielectric constant of the starting materials and especially the volume fraction of the filler is very important. Many theoretical models have been proposed and used for dielectric calculation in comparison with the experimental results. Widely used models including the series, Lichtenecker model, Maxwell-Wagner equation and Kerner expression modified by Jayasundere-Smith (J-S prediction) were calculated. These formulas are described as shown below:

Series model $\qquad \frac{1}{\varepsilon} = \frac{\phi_c}{\varepsilon_c} + \frac{\phi_p}{\varepsilon_p}$ (14)

Lichtenecker model $\qquad \log \varepsilon = \emptyset_p \log \varepsilon_p + \phi_c \log \varepsilon_c$ (15)

Maxwell-Wagner equation $\qquad \varepsilon = \varepsilon_p \dfrac{2\varepsilon_p + \varepsilon_c + 2\emptyset_c(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c - \emptyset_c(\varepsilon_c - \varepsilon_p)}$ (16)

Kerner expression $\qquad \varepsilon = \dfrac{\varepsilon_p \phi_p + \varepsilon_c \phi_c[3\varepsilon_p/(\varepsilon_c + 2\varepsilon_p)][1 + 3\phi_c(\varepsilon_c - \varepsilon_p)/(\varepsilon_c + 2\varepsilon_p)]}{\phi_p + \phi_c(3\varepsilon_p)/(\varepsilon_c + 2\varepsilon_p)[1 + 3\phi_c(\varepsilon_c - \varepsilon_p)/(\varepsilon_c + 2\varepsilon_p)]}$ (17)

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 and ϕ_p are the volume fraction of the ceramic and polymer, respectively (Cho, et al., 2005).