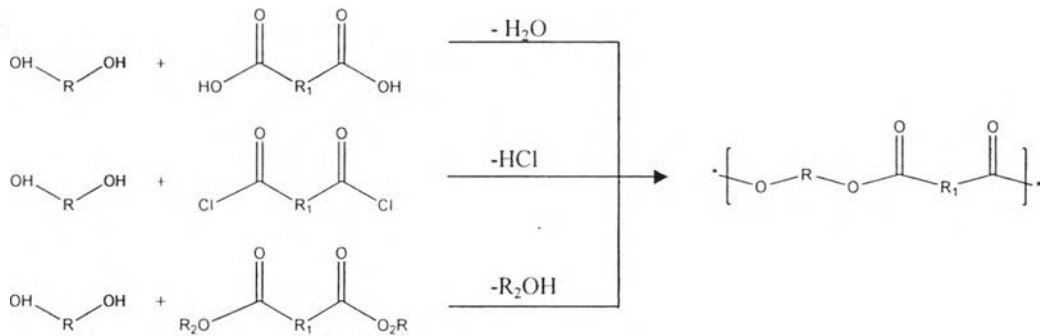


CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Poly(butylene succinate)

Polyesters were the first developed synthetic polymers from condensation polymerization (stepwise polymerization) of difunctional monomers of the AB type (hydroxy acid) or from a combination of AA and BB difunctional monomers. As shown in Schematic 2.1, the polycondensation of difunctional monomers can be categorized into three types; esterification of diacids and diols, diacidchlorides and diols and transesterification of diester and diols.



Schematic 2.1 Preparation of polyesters by stepwise polycondensation (Edlund *et al.*, 2003).

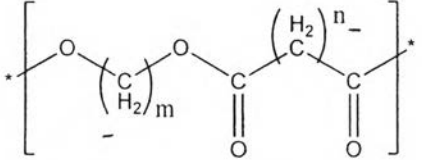
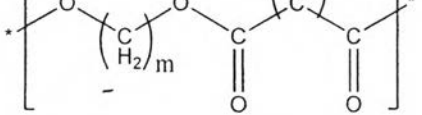

Polyesters are commonly prepared by polycondensation from difunctional monomers such as diols and diacids. They can be inherently degraded by hydrolytic scission of the main chain ester bonds. The inherently degradation of polyester is very attractive for the application of packaging, disposal items and agricultural mulch film (Edlund *et al.*, 2003).

As the major concerns of global warming from increasing plastic wastes, biodegradable polymers are introduced to play an important role in the reduction of plastic wastes. One of the recent development in biodegradable polymers, besides poly(lactic acid) (PLA), is poly(butylene succinate) (PBS).

PBS is classified as aliphatic polyester or poly(alkylene dicarboxylate) which has a common structure as $[O(CH_2)_mOCO(CH_2)_nCO]_x$ when $n = 2,4$ and $m = 2,4$.

The examples of poly(alkylene dicarboxylate) family are shown in Table 2.1 (Ikada *et al.*, 2000).

Table 2.1 Chemical structure of the polymers in poly(alkylene dicarboxylate) family (Ikada *et al.*, 2000).

| Chemical structure : | m | n | Name |
|---|---|---|---|
|  | 2 | 2 | Poly(ethylene succinate) (PES) |
|  | 4 | 2 | Poly(butylene succinate) (PBS) |
|  | 4 | 4 | Poly(butylene succinate-co-butylene adipate) (PBSA) |

The study of poly(butylene succinate) or Bionolle with a high enough molecular weight was first conducted by Fujimaki (1998). Poly(butylene succinate) is the outcome of the combination of 1,4-butanediol and succinic acid via polycondensation reaction. Together with the promising properties which can be comparable to LDPE, PBS is not only soft and strong but also biodegradable (Fujimaki, 1998). Table 2.2 shows the physical properties of PBS compare to those of PLA and several commodity plastics (Ishioka *et al.*, 2002).

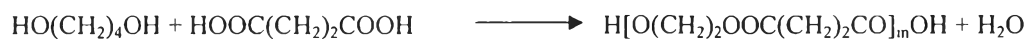
Table 2.2 Properties of PBS compare to those of PLA and some common plastics (Ishioka *et al.*, 2002).

| Items | PLA | PBS | PBSA | PP | HDPE | LDPE |
|-----------------------------------|-----|-------|-------|-----|------|------|
| Glass transition temperature (°C) | 55 | -32 | -45 | -5 | -120 | -120 |
| Melting point (°C) | 175 | 114 | 96 | 163 | 129 | 110 |
| Heat distortion temperature (°C) | 55 | 97 | 69 | 110 | 82 | 49 |
| Tensile strength (MPa) | 66 | 34 | 19 | 33 | 28 | 10 |
| Elongation at break (%) | 4 | 560 | 807 | 415 | 700 | 300 |
| Izod impact strength | 29 | 300 | >400 | 20 | 40 | >400 |
| Degree of crystallinity (%) | - | 35-45 | 20-30 | 56 | 69 | 49 |

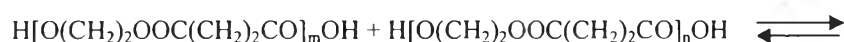
There are two main steps to synthesize poly(butylene succinate). The first step is esterification of succinic acid and 1,4-butanediol or tranesterification of

dimethyl succinate and 1,4-butanediol to obtain oligomers. The second step is polycondensation of oligomers to remove 1,4-butanediol and form high molecular weight PBS (Xu *et al.*, 2010). The reactions are shown below:

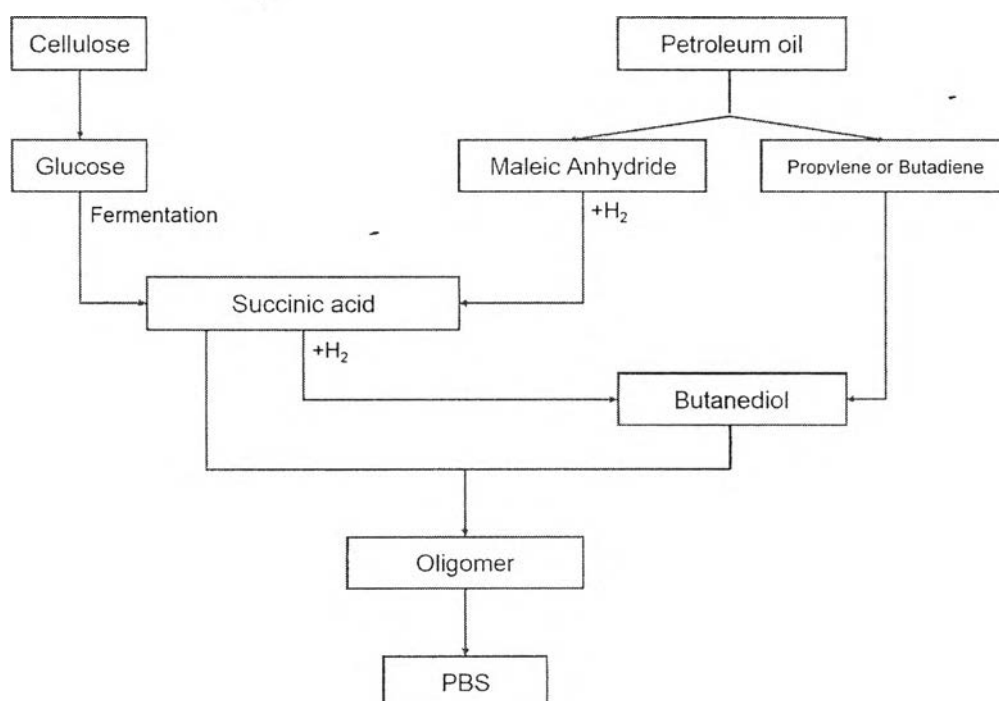
Step 1 :



Step 2 :



The monomers including succinic acid and 1,4 butanediol can be derived from both oil-based and bio-based resources. Generally, succinic acid is produced from hydrogenization of maleic anhydride to succinic anhydride followed by hydration to succinic acid. Additionally, succinic acid can be hydrogenized again to obtain 1,4 butanediol (Xu *et al.*, 2010). The flow chart of the PBS synthesis process is shown in Schematic 2.2.



Schematic 2.2 Flow chart of PBS synthesis (Xu *et al.*, 2010).

PBS is a semicrystalline polyester, whose mechanical properties depend on the degree of crystallinity. There are two type of crystal structures in PBS, alpha (α) and beta (β) form. The α form occurs when PBS is crystallized from a quiescent melt and the β form appears when the mechanical stress is applied. The β form has more extended chain conformation than that of α form, as shown in Figure 2.1. The transition between the α and β form can be reversible when applying and releasing strain (Xu *et al.*, 2010).

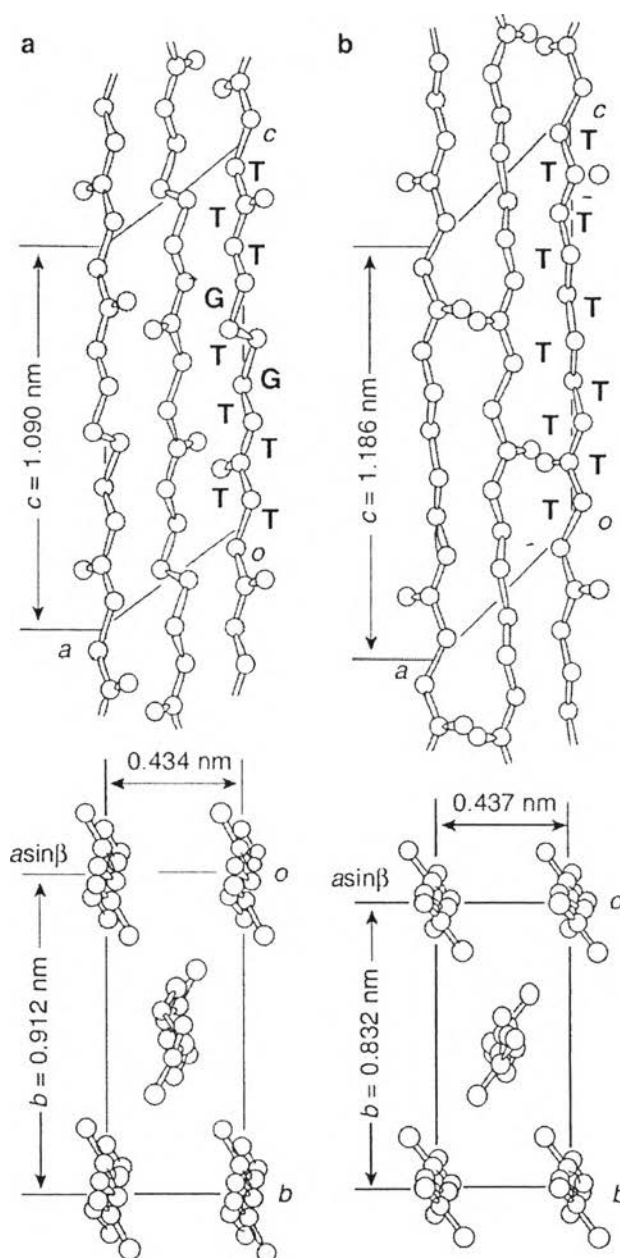


Figure 2.1 Crystal structures of PBS of the a) α form and b) β form (Xu *et al.*, 2010).

In order to improve the performance of poly(butylene succinate), polymer blend of PBS with other biodegradable polymers such as starch, polylactide, polyhydroxybutyrate, etc. were widely investigated (Xu *et al.*, 2010). In 2013, Zhou *et al.* (2013) studied mechanical properties and biodegradability of poly(butylene succinate) by varying the amount of poly(lactic acid) (PLA) in polymer blend system. They discovered the improvement of tensile strength in PBS by increasing the amount of PLA. On the other hand, the elongation-at-break was reduced due to the brittleness of PLA. They also found out that PLA-rich blends decayed faster than PBS-rich blends.

2.2 Dielectric Materials

Dielectric materials or insulators can be classified into two main categories: nonferroelectric (or normal dielectric or paraelectric) materials, which electronic polarization occurs in the application of electric field. And ferroelectric materials, which possess reversible spontaneous polarization over a certain range of temperature (Kao, 2004).

Among those dielectric materials, ferroelectric materials are the most interesting, especially in perovskite-type oxides. The perovskite crystal structure has ABO_3 stoichiometry. The A-site is large rare earth cation and coordinated by 12 anions in the lattice. The B-site is smaller transition cation and coordinated by 6 anions to form octahedral structure (Wodecka-Duś *et al.*, 2007).

Since the early development, the ferroelectric materials are commonly used in capacitor productions. The capacitors are important component in electrical circuit as the feature of blocking, coupling and decoupling, AC-DC separation, energy storage, etc. The capacitance of a capacitor is defined as the dielectric materials which has dielectric constant (ϵ_r) and thickness (d) placed between two parallel metallic plate of area (A), the capacitance is calculated by using the following equation :

$$C = \epsilon_r \epsilon_0 \frac{A}{d} \quad (2.1)$$

where ϵ_0 is permittivity of free space 8.8542×10^{-12} F/m, ϵ_r is dielectric constant of each material, d is thickness of dielectric material, and A is area of electrode.

The capacitors can be categorized into three classes: Class I is the material which has low dielectric constant ranging from 15 to 500, low dielectric losses below $\tan\delta < 0.003$. Class II is the material which has medium to large dielectric constant ranging from 500 to 20,000. The dependence of temperature, electric field and frequency is stronger than those of Class I capacitor. Class III capacitor has similar properties to Class II capacitor, but the working voltage is lower (Kao, 2004).

To select the materials for capacitor production to meet the customer satisfactions, one of most considerate properties of ferroelectric materials is high dielectric constant. Barium titanate was first developed compound used for producing high-dielectric constant capacitors (Haertling, 1999).

2.2.1 Barium Titanate (BaTiO_3)

Barium Titanate is one of the most attractive ferroelectric ceramic which has perovskite structure. However, the unit cell structures are temperature dependent. Which means, at the transition temperature or so-called Curie temperature (T_c), the particular structure can be transformed from one to another. The ferroelectric barium titanate crystal shows a reversible spontaneous electric polarization (P_s) and hysteresis loop can be observed in certain temperature regions below T_c . However, at the temperature above T_c , the crystal is no longer ferroelectric and perform normal dielectric behavior or paraelectric. As show in Figure 2.2(a), the dielectric constant of barium titanate rapidly increases to a very high peak value at T_c of 120°C (Kao, 2004). However, the experiment data exhibits the discontinuous change in polarization-temperature, which the crystal of barium titanate undergoes a first-order transition (Carter *et al.*, 2007), as shown in Figure 2.2(b).

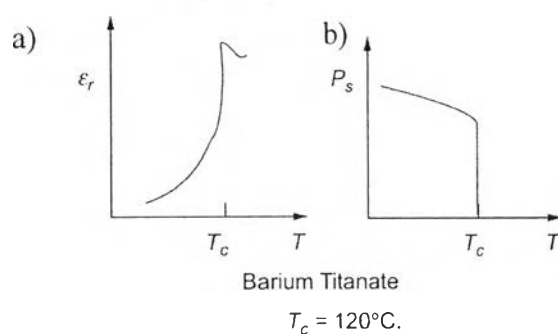


Figure 2.2 The variation of the dielectric constant ϵ_r and the spontaneous polarization of P_s with temperature for barium titanate (Carter *et al.*, 2007).

The symmetrical cubic perovskite structure of barium titanate above T_c is shown in Figure 2.3(a). When the temperature is below Curie temperature (120°C), the positive ions move off-centered positions to form the non-symmetrical tetragonal structure, as shown in Figure 2.3(b). Between 5°C and -90°C the tetragonal structure transforms to orthorhombic structure. The orthorhombic structure will finally transform to rhombohedral structure below -90°C , as shown in Figure 2.3(c) (Kao, 2004).

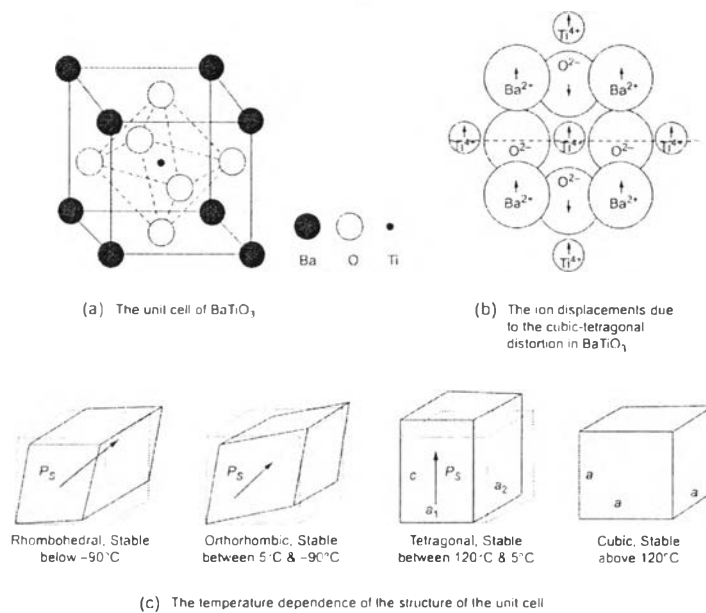


Figure 2.3 The unit cell, the ion displacement and the temperature dependence of the structure of the unit cell of BaTiO_3 (Kao, 2004).

2.2.2 Barium Strontium Titanate ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$)

Barium titanate is rarely used in pure form since high dielectric constant only occurs at high temperature (Carter *et al.*, 2007). The theory of A-site substitution has been introduced in order to modify the ferroelectric behavior of the material. When an A-site ion is replaced with another ion, in the case of barium titanate, the ferroelectric-paraelectric transition temperature can be shifted to lower or higher values. For example, by substituting Ba^{2+} with Sr^{2+} or Pb^{2+} , the Curie temperature (Θ_c) is shifted from lower to upper value respectively (Popovici *et al.*, 2011), as shown in Figure 2.4.

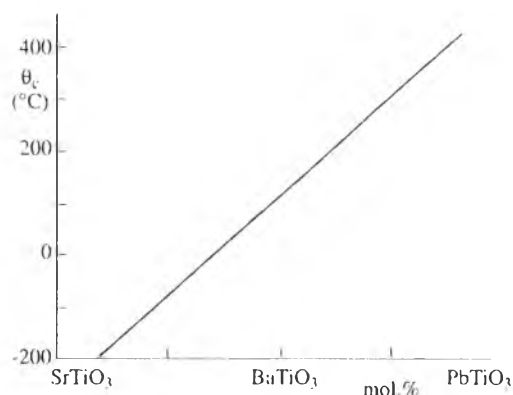


Figure 2.4 The effects on transition temperature by substituting Ba²⁺ with Sr²⁺ or Pb²⁺ (Popovici *et al.*, 2011).

Nowadays, the substitution of Ba²⁺ with Sr²⁺ or Barium Strontium Titanate is one of the most studied solid solution due to its stability and wide range of tunable microwave applications.

Alexandru *et al.* (2004) studied the effect of Strontium concentration at Sr = 0.25, 0.50 and 0.75 mol% in Barium Strontium Titanate solid solution for applications of resonator and phase shifter. The result shows dielectric constant at peak decreases with increasing Sr molar fraction, likewise dielectric losses and Curie temperature significantly decreased. The Curie temperature linearly decreased by the equation $T_c(°C) = 120 - 360x$, when x is strontium fraction. At room temperature, the tetragonality (c_0/a_0) shows tetragonal structure appears only when Sr = 0.25 mol%. On the other hand, the cubic structure of strontium molar fraction equal to 0.50 mol% and 0.75 mol% show paraelectric state. Moreover, the bulk density of barium titanate ceramic in the presence of strontium was studied by Berbecaru *et al.* (2008). The result shows the density slightly decreased with increasing Sr molar fraction.

2.2.3 Magnesium-doped Barium Strontium Titanate (MgO-Ba_{1-x}Sr_xTiO₃)

The idea of doping magnesium in barium strontium titanate ferroelectric material is widely investigated in order to suppress dielectric constants and more importantly, dielectric losses.

Su *et al.* (2004) studied the dielectric behavior of magnesium-doped Ba_{0.8}Sr_{0.2}TiO₃ ceramic by varying the magnesium dopant molar percentages of 0-10%. The result in Figure 2.9 shows that the dielectric constant (permittivity) and loss

tangent (dissipation) decrease significantly at the magnesium molar percentages from 0 to 2, as shown in Figure 2.5. Additionally, the tetragonality decreased from 1.004 to almost 1.000, which affected to transformation from tetragonal to cubic structure and showed a significantly drop in Curie temperature from 66°C to -30°C.

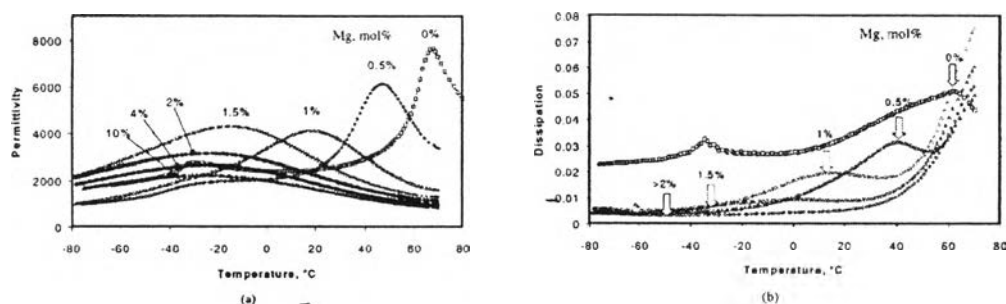


Figure 2.5 Dielectric properties of Ba_{0.8}Sr_{0.2}TiO₃ ceramic with different Mg-dopant concentrations (Su *et al.*, 2004).

Five years later, Xu *et al.* (2009) investigated the microstructure of magnesium-doped Ba_{0.65-x}Sr_{0.35}Mg_xTiO₃ ceramic. In Figure 2.6, the XRD results show significantly drop in the lattice constant when the molar percentage of magnesium (x) increased from 0 to 0.5, which means that the reduction of the lattice constant occurred when Mg²⁺ occupies in the A-site of perovskite ABO₃ structure, as shown in Figure 2.7(a). When the concentration of magnesium is between 1.0 mol% and 3.5 mol%, the lattice constant gradually increases due to the replacement of Mg²⁺ in the B-site titanium ion, as shown in Figure 2.7(b). However, when the magnesium concentration above 3.5 mol%, the lattice parameter starts to decrease again due to the Mg²⁺ equivalent dopant, as shown in Figure 2.7(c).

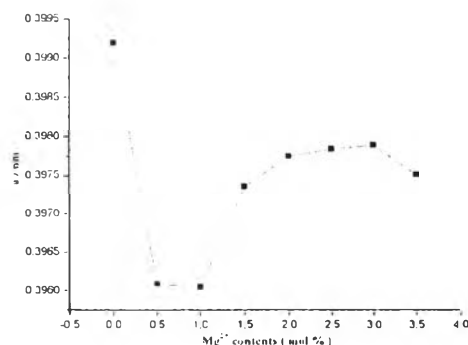


Figure 2.6 Mg²⁺ content dependent of lattice constant of Ba_{0.65-x}Sr_{0.35}Mg_xTiO₃ ceramic (Xu *et al.*, 2009).

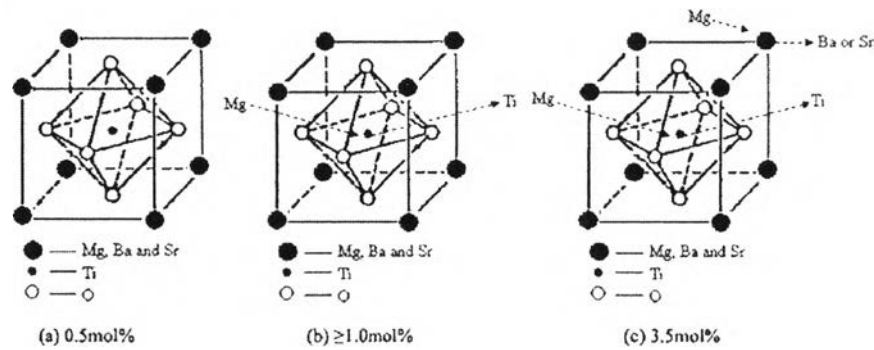


Figure 2.7 The effect of Mg^{2+} with different content on the perovskite ABO_3 structure (Xu *et al.*, 2009).

2.2.4 Ceramic Powder Preparation

To date, the fabrication of barium titanate and barium strontium titanate ceramics have been typically prepared by conventional mixed oxide method or solid state reaction (Wodecka-Duś *et al.*, 2007). Besides, the sol-gel process has attracted in some field, such as, the fabrication of multicomponent oxides ferroelectric films, bulk powders and ceramics due to the ease of process, low processing temperature and fine particle size. Sharma *et al.* (1993) also claimed that high quality $BaTiO_3$ ceramic could be obtained by sol-gel process.

Shiibashi *et al.* (1999) successfully synthesized barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$) ceramic by sol-gel method using metal alkoxide as precursors. They also studied the lattice parameter decreases as increasing strontium molar contents (x), which affected to the reduction of Curie temperature.

Somani *et al.* (2007) identified the sequence of phase evolution during the calcination in sol-gel process of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic powder using barium acetate, strontium acetate and titanium (IV) isopropoxide as precursors. The chemical equation leading $Ba_{1-x}Sr_xTiO_3$ phase evolution could be written as:



2.3 Polymer-Ceramic Composites

The concept of using composite materials in electronic industry was first proposed by Newnham *et al.* (1978). Instead of using only one phasic materials, the optimized combination of materials could be used in order to introduce more than one properties into the material. Especially, for polymer-ceramic composite, the flexibility and formability of polymeric materials can be combined with high dielectric constant of ferroelectric ceramic to compensate the brittleness nature of ceramic materials. Not only choosing the right materials for a specific usage, but also concerning about how to couple them with the best possible design structure (Dias *et al.*, 1996).

The connectivity approach was also invented by Newnham *et al.* (1978) in order to develop the property of multiphase solid, which was mentioned that each phase in a composite may be zero, one, two or three dimensions self-connected. There are ten combinations of connectivity in diphasic system; 0-0, 1-0, 2-0, 3-0, 1-1, 2-1, 3-1, 2-2, 3-2, and 3-3, which can be visualized in Figure 2.8.

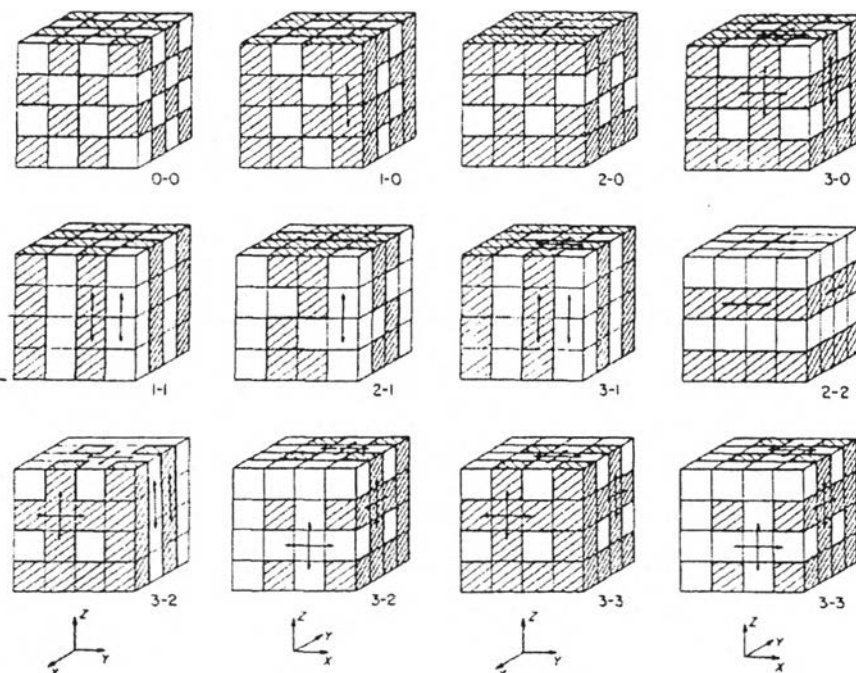


Figure 2.8 Ten connectivity patterns for a diphasic solid (Newnham *et al.*, 1978).

The 3-0 (or 0-3) composites are the most commonly studied polymer-ceramic composites formed by dispersing 0-dimensional ceramic powders into 3-dimensional continuative polymer matrix (Fang *et al.*, 2009). There are four possible approaches in order to increase dielectric constant (ϵ_r) of the composite; the content of the filler, improving the polymer-ceramic interfaces, drying the materials before processing, or adjusting the morphology of the filler grains. Although, by increasing the filler content may affect to poor fluidity, flexibility and low strength in the composite (Sebastian *et al.*, 2010).

To predict dielectric constant of the composite, the mixing rules has been purposed as the function of dielectric constant and volume fraction of filler. There are four equations commonly used (Moulson *et al.*, 2003) :

Parallel mixing rule:

$$\epsilon_m = (1 - V_f)\epsilon_2 + V_f\epsilon_1 \quad (2.2)$$

Series mixing rule:

$$\epsilon_m^{-1} = (1 - V_f)\epsilon_2^{-1} + V_f\epsilon_1^{-1} \quad (2.3)$$

Maxwell's mixing rule:

$$\epsilon_m = \epsilon_2 \left\{ 1 + \frac{3V_f(\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\epsilon_2 - V_f(\epsilon_1 - \epsilon_2)} \right\} \quad (2.4)$$

Lichtenecer's mixing rule:

$$\ln \epsilon_m = \sum V_f \ln \epsilon_i \quad (2.5)$$

where ϵ_1 is dielectric constant of filler phase, ϵ_2 is dielectric constant of matrix phase, and V_f is volume fraction of fillers.

2.3.1 Dielectric Properties of Polymer-Barium Titanate Composite

The investigation on barium titanate or barium strontium titanate – polymer composite has been widely studied due to their high dielectric constant with the lead-free special feature for environmental protection (Fang *et al.*, 2009). The various type of polymer matrix has been investigated in order to optimize the condition of usage, such as the dielectric properties as the function of working frequency and temperature.

The good example of thermoplastic-barium titanate composite is the work of Popielarz *et al.* (2001). The dielectric properties of three polar polymer

including; Trimethylolpropane triacrylate (TMPTA), Poly(ethylene glycol)diacrylate (PEGDA) and 1,14-tetradecanediol dimethacrylate (TDDMA) were studied. The result show that the dielectric constants (ϵ_r) and loss tangent ($\tan\delta$) were polarity dependent, the polarity and dielectric properties are ranging from minimum to maximum by TDDMA<TMPTA<PEGDA. The polarity was depended on the amount of C-O bond in polymer structure. Also, the frequency dependent dielectric properties of composite materials shows the reduction of dielectric constant as the frequency decreased. However, the composite materials shows increasing in loss tangent with increasing the frequency, as shown in Figure 2.9. It was suggested that, by using at high frequency range, the low polar polymer performs better than those high polar polymer. Furthermore, Figure 2.10 shows the dielectric constant of the composites increases as the volume fraction of BaTiO₃ increases.

The relationship between dielectric constant and volume fraction of BaTiO₃ followed the Modified-Lichtnecker's mixing rule, as show in the following equation:

$$\log \epsilon'_{composite} = \log \epsilon'_{matrix} + V_f \log \left(\frac{\epsilon'_{filler}}{\epsilon'_{matrix}} \right) \quad (2.6)$$

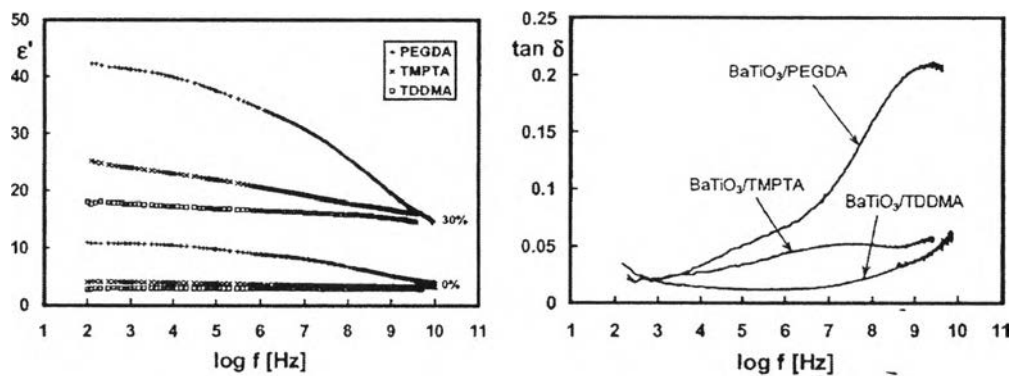


Figure 2.9 Comparison of the frequency characteristic of dielectric constant and loss tangent of 30% BaTiO₃/polymer composites (Popielarz *et al.*, 2001).

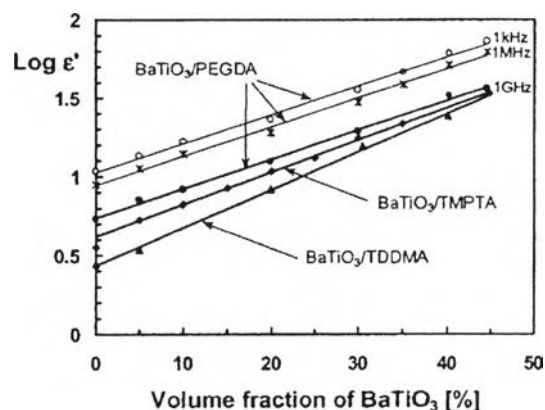


Figure 2.10 Dielectric constant of the composite material as the function of volume fraction of BaTiO₃ (Popielarz *et al.*, 2001).

In 2007, Hu and coworker had successfully developed high frequency dielectric polymer-ceramic composites for wireless telecommunication applications. The barium strontium titanate ceramic powder in the composition of 30, 42, 50, and 60 wt% were loaded in polyphenylene sulfide (PPS) polymer matrix. The measurement of dielectric constants and loss tangent with an impedance analyzer. The result showed that even at high frequency, the composite still exhibit low loss tangent, which is very good for high frequency application. Most importantly, the relationship between dielectric constant and BST filler loading are perfectly fit to modified Lichtenecker mixing rule, as shown in Figure 2.11 (Hu *et al.*, 2007).

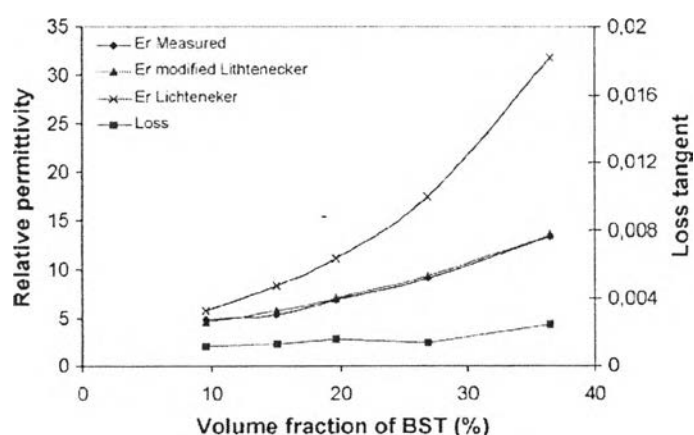


Figure 2.11 Dielectric constant of the PPS-BaTiO₃ composite material as the function of volume fraction of BaTiO₃ (Hu *et al.*, 2007).

The preceding developments of high frequency dielectric properties in the composite of barium titanate and barium strontium titanate filler loading in various type of polymer matrix are summarized in Table 2.3.

Table 2.3 Comparative data of the investigations on polymer-ceramic composite dielectric properties at room temperature

| Polymer | Filler | V_f | ϵ_r | $\tan\delta$ | freq. (Hz) | Reference |
|---|--|-------|--------------|--------------|------------------|---------------------------------|
| Polyvinylidene fluoride (PVDF) | BaTiO ₃ | 0.7 | 45.0 | 0.3500 | 10 ⁶ | Muralidhar <i>et al.</i> (1987) |
| Poly(ethylene glycol)diacrylate (PEGDA) | BaTiO ₃ | 0.3 | 35.0 | 0.0700 | 10 ⁶ | Popielarz <i>et al.</i> (2001) |
| Trimethylolpropane triacrylate (TMPTA) | BaTiO ₃ | 0.3 | 21.0 | 0.0400 | 10 ⁶ | |
| 1,14-tetradecanediol dimethacrylate (TDDMA) | BaTiO ₃ | 0.3 | 16.0 | 0.0200 | 10 ⁶ | |
| Cyanoethylated cellulose polymer (CR-S) | BaTiO ₃ | 0.3 | 51.0 | 0.0186 | 10 ⁶ | Chiang <i>et al.</i> (2002) |
| Poly(vinyl chloride) (PVC) | BaTiO ₃ | 0.4 | 21.0 | 0.0190 | 10 ⁵ | Olszowy <i>et al.</i> (2005) |
| Polyimide (PI) | BaTiO ₃ | 0.5 | 35.0 | 0.0257 | 10 ⁴ | Xie <i>et al.</i> (2005) |
| Polyaniline (PANI) | BaTiO ₃ | 0.5 | 5.0 | 0.2000 | 10 ¹⁰ | Pant <i>et al.</i> (2006) |
| Polyphenylene sulfide (PPS) | Ba _{0.55} Sr _{0.45} TiO ₃ | 0.7 | 13.5 | 0.0025 | 10 ⁹ | Hu <i>et al.</i> (2007) |
| Cyclic olefin copolymer (COC) | Ba _{0.5} Sr _{0.5} TiO ₃ | 0.3 | 9.5 | 0.0015 | 10 ² | Hu <i>et al.</i> (2007) |
| Polypropylene-graft-poly(styrene-stat-divinylbenzene) | Ba _{0.55} Sr _{0.45} TiO ₃ | 0.5 | 28.0 | 0.0080 | 10 ⁹ | Sonoda <i>et al.</i> (2010) |

2.3.2 Dielectric Properties of Poly(Butylene Succinate) Composite

The idea of using biodegradable polymer in electrical application has been conducted since the environmental pollution became the serious problem. Started from the group of Nakagawa *et al.* (2004), they successfully developed polylactic acid (PLA) film as an insulator which has dielectric properties almost the same as crosslinked-polyethylene (XLPE), but the impulse breakdown strength is greater than XLPE. Following by the development of PLA-insulated electric cable, which was invented by Nakiri *et al.* (2007).

Therefore the investigation on the dielectric properties of some biodegradable polymers has been conducted such as poly-L-lactic acid (PLLA),

polyethylene terephthalate succinate (PETS), polycaprolactone butylene succinate (PCL-BS), polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), and polyhydroxybutyrate/valerate (PHB/V) compared to low density polyethylene (LDPE) in the application of insulator. The result in Table 2.4 shows the biodegradable polymer have tendency to have higher dielectric constant than that of LDPE which can be explained by the presence of carbonyl groups in the structure (Ohki *et al.*, 2007).

Table 2.4 Values of thermal properties, dielectric constant and Impulse breakdown strength of biodegradable polymers (Ohki *et al.*, 2007)

| Materials | T _g (C) | T _m (C) | Dielectric constant at 1 kHz | Impulse breakdown strength (MV/cm) |
|-----------|--------------------|--------------------|------------------------------|------------------------------------|
| PLLA - | 65 | 166 | 2.71 | 6.29 |
| PCL-BS | 50 | 205 | 5.10 | 4.03 |
| PETS | -60 | 95 | 3.04 | 3.96 |
| PBS | -32 | 111 | 4.63 | 4.14 |
| PBSA | -45 | 92 | - | 3.48 |
| PHB/V | < 25 | 146 | - | 3.13 |
| LDPE | -30 | 113 | 2.25 | 3.56 |

Poly(butylene succinate) is one of the most admirable biopolymer. However, there have been several investigations regarding dielectric properties of neat-PBS and PBS-composite.

The first investigation on dielectric spectroscopy of neat-PBS thin film was conducted by Tai (2007). The results showed that when temperature change, the polymer undergoes α and β relaxation depended on the way of molecular packing. In addition, as the temperature increases, the material exhibit higher dielectric behaviors. Also, as the frequency decreases, the dielectric constant decreases due to the material exhibit various type of polarization.

However, the dielectric properties of neat-PBS are still low. Therefore, the inspiration on improving dielectric properties of poly(butylene succinate) by introducing high-dielectric-constant fillers which have been conducted by Yu *et al.* (2011). The filler used in the composite is polyaniline (PANI) powder, the obtained composite was claimed to be all-organic nanocomposite for the capacitor application.

The result shows the increment of dielectric constant as the filler increases. For the filler volume fraction below 20%, the relationship of dielectric constant followed percolation theory. There are three components involved in this theory including matrix, fillers and interphases. The other idea in dielectric PBS-composite was conducted by the group of Yu *et al.* (2012), the filler used in the composite is natural graphite (NG). The results showed the excellent dispersion of filler phase, this factor have led to the improvement of dielectric properties. This study also fit to the percolation theory.

The overall investigations on the dielectric properties of PBS-composite material are summarized into Table 2.5. However, the improvement of dielectric properties of PBS-composite are needed to be further studied.

Table 2.5 Comparative data of the investigations on PBS-composite dielectric properties at room temperature

| Polymer | Filler | V_f | ϵ_r | $\tan\delta$ | freq. (Hz) | Reference |
|--------------------------------|-----------------------|-------|--------------|--------------|------------|-------------------------|
| Poly(butylene succinate) (PBS) | - | - | 4.8 | 0.025 | 10^6 | Yu <i>et al.</i> (2011) |
| | Polyaniline (PANI) | 17.5 | 20 | 0.180 | 10^6 | Yu <i>et al.</i> (2011) |
| | Natural graphite (NG) | 5.5 | 27 | - | 10^6 | Yu <i>et al.</i> (2012) |