

CHAPTER II

LITERATURE REVIEW

2.1 Benzoxazine

In recent years, processing of thermosetting resins has received strong attention from the automotive, aerospace and construction industries because of the great potential of these materials. These novel phenolic resins are based on benzoxazine structures, which were first synthesized by Holly and Cope (Holly and Cope, 1944). These structures were not recognized as phenolic resin precursors until Schreiber reported in 1973 that a hard and brittle phenolic material was formed from benzoxazine precursors (Schreiber, 1973). No further details about structures and properties were included. Later, Riess et al studied the synthesis and reactions of monofunctional heterocyclic compounds of this kind. They found that only oligomeric phenolic structures could be obtained because the thermodissociation of the monomer was always competing with the chain propagation (Riess et al, 1986). Polyfunctional benzoxazine monomers have been used as modifiers for coating and encapsulation (Ishida, H., Rodriguez, Y., 1995). Ning and Ishida synthesized difunctional benzoxazine precursors (Ning, X., and Ishida, H., 1994) to overcome the low degree of cure the compounds prepared by Riess et al. The curing reaction of the benzoxazine precursors is an autocatalysed reaction (Ishida, H., and Rodriguez, Y., 1995) and they presented the first step towards developing a new class of phenolic materials; the synthesis and characterizations of phenolic resin precursors through the use of difunctional or multifunctional benzoxazine compounds, and their curing into phenolic materials with the ring-opening reaction being initiated by the dimers and higher oligomers in the resin composition. Result is this family of compounds offer greater flexibility than conventional novolac or resole resins in terms of molecular design. It is also superior to conventional phenolic resin in process control since it releases no by-product during curing reactions (Ning, X., and Ishida, H., 1994). The physical and mechanical properties of these new polybenzoxazines are investigated

and are shown to compare very favorably with those of conventional phenolic and epoxy resins. Two phenolic polybenzoxazines have demonstrated the potential of this new class of resins as high-temperature, high-strength matrix materials. The ring-opening polymerization of these new materials occurs with either near-zero shrinkage or even a slight expansion upon cure. The polybenzoxazines may be ideally suited for high-performance adhesives and composites that can be produced with little internal stresses. Dynamic mechanical analysis reveals that these candidates for composites applications possess high moduli and glass transition temperatures, but low crosslink densities. Long term immersion studies indicate that these materials have a low rate of water absorption and low saturation content. Impact, tensile, and flexural properties are also studied. Results of the dielectric analysis on these polybenzoxazines demonstrate the suitability of these materials for electrical applications (Ishida, H., and Allen, D.J., 1996A). Furthermore, the benzoxazines are copolymerized with an epoxy resin in order to modify their performance. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. Copolymerization leads to significant increases in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness (Ishida, H., and Allen, D.J., 1996B). The ring-opening polymerization of benzoxazines using a weak carboxylic acid as catalyst is likely to be an auto-accelerated reaction. This auto-accelerated reaction is in contrast to the reaction that occurs with strong acids as catalysts where there is no lag between the ring-opening and the Mannich bridge formation reactions (Dunkers, J., and Ishida, H., 1998). Acetylene-functional benzoxazines polymerized in air resulted in higher char yield and thermal stability than those polymerized under an inert atmosphere, due to the different concentration and structure of newly formed polyene chains by acetylene group polymerization, and due to the different extent of ring-opening polymerization. Polymerization of both oxazine and acetylene groups proceeds faster and to a greater extent under an air environment (Kim, H.J. et al, 1999). Molecular modeling results show that the oxazine ring in a

benzoxazine molecular assumes a distorted semi-chair structure in terms of minimum energy model. The resulting ring strain makes it possible for this kind of molecule to undergo ring-opening polymerization under certain reaction conditions. Moreover, the strong basicity of the N and O atoms by Lewis definition makes the ring very likely to be opened via a cationic mechanism (Wang, Y.X., and Ishida, H., 1999). With certain cationic initiators, benzoxazine rings can be opened and polymerized at room temperature, with high glass transition temperature and high char yield under nitrogen environment were produced. Low-viscosity ternary mixtures of benzoxazine, epoxy and phenolic resins have been developed. The blends render homogeneous and void-free cured specimens with a wide range of properties which are highly dependent on the composition of the starting resins in the ternary mixture. Benzoxazine resin imparts thermal curation, low water uptake, high char yield, and mechanical strength to material while epoxy is used mainly to reduce the viscosity of the mixture for special applications. Besides the function as a diluent, epoxy resin also gives higher crosslink density material with improved thermal stability as well as lowers the ambient temperature modulus of the ternary systems. Curing retardation and higher water absorption are the adverse effects from the use of epoxy as a diluent. Finally, phenolic novolac acts as a curing accelerator to the systems, aside from its typical function as a hardener of epoxy resin. The transition temperature was found to be strongly dependent on the combined amount of benzoxazine and epoxy resins in the ternary systems (Rimduisit, S., and Ishida, H., 2000).

2.2 Piezoelectric Ceramic

Piezoelectricity is a phenomenon exhibited by noncentrosymmetric crystals whereby an electric polarization (i.e. charge) is induced in the material upon the application of a stress. Conversely, it is the development of an induced strain which is directly proportional to an applied electric field. Piezoelectric materials are green energy

materials and they perform well over a wide temperature range and resist damage from severe shock and/or vibration (Tressler, J.F., et al, 1998).

Hu-Yong Tian et al. studied the BST graded films at low temperatures below 750°C and investigated the structure and optical properties of the graded thin films. Results from the Auger depth profile showed that no obvious oxygen deficiency was present in the surface layer. XRD measurements were also consistent with the presence of a range of compositions in the films rather than discrete layers of BaTiO₃ and SrTiO₃. Graded BST films were crystallized at 730°C consisting of a pseudo-cubic, or perovskite phase, while having no preferred orientation. The crystalline phase of the graded BST thin film is different from that of BaTiO₃ and SrTiO₃.

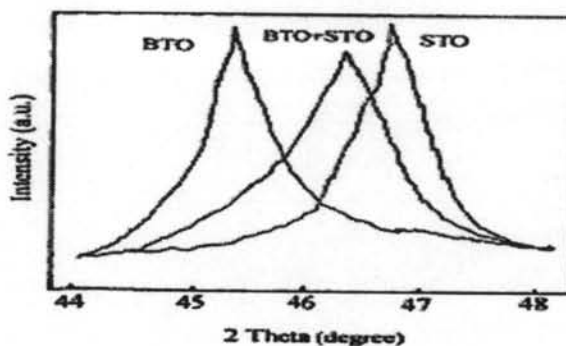


Figure 2.1 XRD pattern showing (200) peaks of BaTiO₃(BTO), SrTiO₃(STO), and the graded BST(BTO/STO)film with 2θ in 44–48°.

From Figure 2.1, it is seen that the position of the XRD peaks for BST(Ba/Sr) shift with composition. It is verified by the two distinct peaks at $2\theta \sim 45.4^\circ$ for BaTiO₃ and $2\theta \sim 46.7^\circ$ for SrTiO₃, respectively. The peak from the graded BST thin film, however, is broad and centered at $2\theta \sim 46.7^\circ$, which is consistent with a film having a graded region with a linear Ba/Sr ratio (Tian, H.Y., et al, 2001A).

(Ba_xSr_{1-x})TiO₃ is the solid solution of BaTiO₃ and SrTiO₃, which belongs to the general class of ferroelectric materials based on the perovskite structure. Since the solid

solution can be formed over the whole concentration range, electrical and optical properties of maybe tailored continuously with a molar ratio from 0 to 1 (Tian, H.Y. et al, 2001A). Especially $B_{0.5}S_{0.5}TiO_3$ thin film in paraelectric phase, which have characteristics such as good chemical and thermal stability and good insulating properties, are often considered the most suitable capacitor dielectrics for successful fabrication of high density Gbit scale DRAMS. $Ba_xSr_{1-x}TiO_3$ (BST) is paid more attention because of its unique combination of large dielectric constant, low direct current (DC) leakage, low loss tangent, and stable operation at high temperature (Subbarao, E.C., 1998).

Developments in solid state chemistry made it possible to prepare compositions with unsurpassed homogeneity and mixing on an atomic scale, by the sol-gel route from alkoxides and other precursors. One other advantages of the solution methods of powder preparation is the extremely small particle size of the resulting materials, which in turn lowers the sintering temperature, sometimes by as much as a few hundred degrees. For example, chemically prepared zirconia can be sintered to high density at $1400^\circ C$, a temperature substantially lower than that required for material prepared by conventional methods. Uniform distribution of small quantities of a dopant is facilitated by the sol-gel route, as in the incorporation of about 0.3% of lanthanum or other rare earth oxides in barium titanate to decrease its electrical resistivity by about 10 orders of magnitude. The semiconducting barium titanate with a room temperature electrical resistivity of about $100 \Omega cm^{-1}$ exhibits a sharp rise in electrical resistivity by four to six orders of magnitude in the vicinity of its curie temperature. The magnitude and sharpness of the resistivity change, on which a number of control applications are based, is determined by the homogeneity of dopant distribution and by the grain size (Lee, H.G., Kim, and H.G., 1990). The effect of grain size on the dc field dependence of dielectric characteristics in $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics prepared by a sol-gel method was studied. $Ba_{0.6}Sr_{0.4}TiO_3$ with different grain sizes was prepared by sol-gel method with different sintering temperature and time. The influence of the dc field on the loss factor is much less than that on the

dielectric constant. As the grain size increases, the maximum dielectric constant and the percentage change of dielectric constant under a dc field increase (Jiwei, Z. et al, 2002).

2.3 Polybenzoxazine Composites

Piezoelectric ceramics, such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and BaTiO_3 , are used extensively as transducer materials. However these materials have limited utility in electromechanical transducers used under hydrostatic conditions because of their low hydrostatic piezoelectric coefficients, high permittivities, and high densities which are unsuitable for acoustic matching with water. One approach to these problems is with composite bodies made from piezoelectric ceramics and polymers. The polymer phase lowers the density and permittivity and increases the elastic compliance of composites. If the properties of the piezoelectric composite change with ceramic particle size, it is important to choose the proper particle size in order that the composite may have maximum properties (Abdullah, M.J., and Dass-Gupta, D.K., 1990). Ferroelectric composites of ceramic and polymer lately have received considerable attention due to their advantages in piezoelectric properties for transducer applications. These composites thus constitute a new structure which might combine a high ferroelectric activity of ceramics and high mechanical strength of polymers. Obviously, the design of the composites with optimum properties becomes very challenging since the electro-active properties do not only depend on the materials and the compositions but also on their interconnections (Huber, C. et al, 2004).

The need for functional materials in numerous fields of applications, biology, nanotechnology, electronics, has stimulated the research in the design of tailored materials. Obtaining such specially designed materials in view to control and then to predict their properties requires complex synthesis, improvement of shaping and refinement of the final properties modeling. In the field of ferroelectric materials, some attempts to elaborate tailored composite materials can be reported from the literatures. Ceramic and sol-gel synthesis routes are mostly used. To process agile high frequency

devices such as tunable resonators or phase shifters, the challenge is to decrease the dielectric losses of the material, keeping an sensitivity of the permittivity with the electric field. $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ [BST(1-x)-x] based composites including a dielectric phase (MgO, MgTiO₃, . . .) are promising candidates. Most of them have been obtained by solid state route. C. Huber, et al. studied on nanosized ferroelectric powders have been encapsulated in a thin surrounding shell made of a binary oxide. The conservation of the ferroelectric transition in the composite has been shown while preserving the size of the ferroelectric cores after sintering (Huber, C., et al, 2004).

Ishida and Rimdusit reported the use of low melt viscosity polybenzoxazine filled with boron nitride ceramics to improve the composite thermal conductivity. The resulting materials show an extraordinarily high thermal conductivity value. The molding compound exhibited high and stable mechanical strength up to 200°C and low water absorption (Ishida, H., and Rimdusit, S., 1998). Jang and Yang studied the effects of surface treatments, such as oxygen plasma and nitric acid treatment, on the mechanical properties of carbon fiber (CF)/polybenzoxazine composites and resulted oxygen plasma treatment and nitric acid treatment were effective in improving the mechanical properties of CF/polybenzoxazine composites (Jang, J., and Yang, H., 2000). An immiscible polymer-clay nanocomposite has been synthesized by Phiriyawirut et al. which consisting of dispersed layers of organically modified montmorillonite (OMOM) in a polybenzoxazine matrix. The results suggested that the compatibility between amine modifying agents and benzoxazine played the most important role for the characteristics of the nanocomposite (Phiriyawirut, P. et al, 2001).