

CHAPTER I

INTRODUCTION

Polymer composites are important commercial materials with many applications. In recent years, however, we have reached the limits of optimizing composite properties of traditional micrometer-scale composite fillers, because the properties achieved usually involve compromises (Ajayan, P.M. et al, 2003). Recently, research and development of nano-filled polymers have greatly increased, for example in the textile, automotive and plastic industries. One of the reasons why nanocomposites are interesting is nanocomposites can greatly improve both chemical and physical properties of polymer matrices by using only small amounts of nano-size fillers (Ning, X., and Ishida, H., 1994). 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 (Abdullah, M.J. et al, 1990)

In this study, the novel polymer nanocomposite between a piezoelectric ceramic and a polymer is of main interest. Polybenzoxazine (Figure 1.1) is used as the polymer matrix because of the advantages over the traditional phenolic resins. Polybenzoxazine has been developed from traditional phenolic resins. Phenolic resins have good heat resistance and the raw materials are very inexpensive but upon curing, phenolic resins have high volumetric shrinkage. Polybenzoxazine has good heat resistance and it is also superior to conventional phenolic resin in process control since it releases no by-products during curing reactions (Ning, X., and Ishida, H., 1994) and its shrinkage is near zero (Ishida, H., and Allen, D.J., 1996). Usually phenolic resins were used as polymer substrate in electronic applications. Upon the study investigating the dielectric

properties of polybenzoxazine composite with a well known piezoelectric ceramic would bring the opportunity for polybenzoxazine to substitute the conventional phenol resins. Rather than that the novel polymer nanocomposite could show a great potential to use this material in electric application at microwave frequency range.

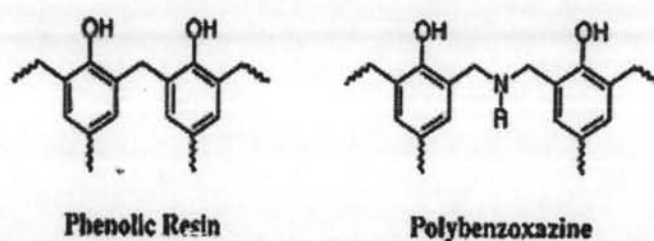


Figure 1.1 Structure of phenolic resins and polybenzoxazines (Hemvichian, K. et al, 2001).

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). In this study, barium strontium titanate (BST, $Ba_{1-x}Sr_xTiO_3$) is mixed with polybenzoxazine to make a piezoelectric ceramic polymer composite.

Barium strontium titanate $Ba_{1-x}Sr_xTiO_3$ (BST) (Figure 1.2) is a continuous solid solution of ferroelectric $BaTiO_3$ and paraelectric $SrTiO_3$. As a result, the curie temperature of BST linearly decreases with increasing Sr concentration. The transition temperature and hence the properties of BST, can be tailored by changing the composition according to the requirements of the specific applications (Nayak, M. et al, 2002). $(Ba_{1-x}Sr_x)TiO_3$ is of high interest since it provides a unique combination of high dielectric constant, low DC leakage, low loss tangent up to high frequencies, and stable operation at high temperatures (Wu, D. et al, 2000).

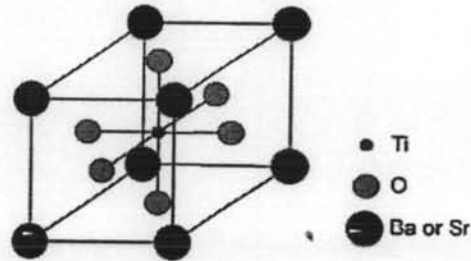


Figure 1.2 Structure of Barium Strontium Titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST).

A number of methods, including sol-gel processing, metal-organic decomposition (MOD), rfsputtering, pulsed laser deposition (PLD), metal-organic chemical vapor deposition (MOCVD), etc., have been applied to synthesize ceramic materials. Among them, sol-gel processing shows attractive advantages over the others for the fact that particles with extremely uniform composition over large areas can be obtained with simple non-vacuum equipment (Tian, H.Y., et al, 2001). Moreover, the Sol-Gel process allows to synthesize ceramic materials of high purity and homogeneity by means of preparation techniques different from the traditional process of fusion of oxides and the fundamental property of the sol-gel process is that it is possible to generate ceramic material at a temperature close to room temperature (C. J. Brinker and G. W. Scherer, 1990).

To date, no papers have reported on preparing BST in nanoscale to mix with polybenzoxazine. In this research work, BST will be prepared in nanoscale using sol-gel process in order to obtain good dispersion and distribution of BST when mixing it with polybenzoxazine. Moreover, BST will be prepared in ceramic form in order to measure the properties of ceramic to compare with polybenzoxazine and polymer nanocomposite. The electrical and thermal properties of a novel nanocomposite, BST and polybenzoxazine will be studied.

1.1 Benzoxazine

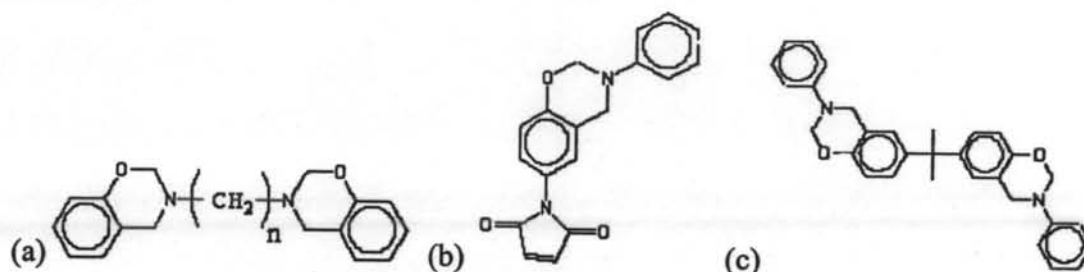


Figure 1.3 (a), (b) and (c) Structures of benzoxazine monomers.

The benzoxazine (Figure 1.3) is a single benzene ring fused to another six-membered heterocycle containing one oxygen atom and a single nitrogen atom. There are a number of possible isomeric benzoxazines depending on the relative positions of the two heteroatoms and the degrees of oxidation of this oxazine ring system. As a specific kind of hydrogenated benzoxazine, 3-substituted-3,4-dihydro-2H-1,3-benzoxazine was studied mainly as an alternative product of the Mannich reaction. This type of benzoxazine was found as a new type of precursor of phenolic resin. Some of polybenzoxazine materials have excellent physical and mechanical properties as well as processability (Liu, J., and Ishida, H.). The precursors are formed from phenol and formaldehyde in the presence of amines. The choice for phenol and amine permits design flexibility and polymer property tailoring. The ring-opening polymerization can be catalyzed by acidic catalysts that permit a widely cure temperatures (Nair, C.P.R., 2004).

These new materials, belonging to the additional cure phenolics family, were developed to combine the thermal properties and flame retardance of phenolics and the mechanical performance and molecular design flexibility of advanced epoxy systems. The polybenzoxazine overcomes several short-comings of conventional novolac-type and resole-type phenolic resins, while retaining their benefits. Polybenzoxazine resins are expected to replace traditional phenolics. The physical and mechanical properties of these new polybenzoxazines are shown (Table 1.1) to compare very favorably with those

of conventional phenolic and epoxy resins. The resin permits development of new applications by utilizing some of their unique features such as:

- Near zero volumetric change upon polymerization
- Low water absorption
- T_g much higher than cure temperature
- Fast mechanical property build-up as a function of degree of polymerization
- High char-yield
- Low coefficient of thermal expansion (CTE)
- Low viscosity
- Excellent electrical properties (Nair, C.P.R., 2004).

Table 1.1 Comparative properties of various high performance polymers

Property	Epoxy	Phenolic	Toughened BMI	Bisox- phen (40:60)	Cyanate ester	P-T resin	PBZ
Density (g/cc)	1.2-1.25	1.24-1.32	1.2-1.3	1.3	1.1-1.35	1.25	1.19
Max use temperature (°C)	180	200	~200	250	150-200	300-350	130-280
Tensile strength (MPa)	90-120	24-45	50-90	91	70-130	42	100-125
Tensile modulus (GPa)	3.1-3.8	03/05	3.5-4.5	4.6-5.1	3.1-3.4	4.1	3.8-4.5
Elongation (%)	3-4.3	0.3	3	1.8	02/04	2	2.3-2.9
Dielectric constant (1 MHz)	3.8-4.5	04/10	3.4-3.7	-	2.7-3.0	3.1	3-3.5
Cure temperature (°C)	RT-180	150-190	220-300	178-225	180-250	177-316	160-220
Cure shrinkage (%)	>3	0.002	0.007	<1	~3	~3	~0
TGA onset (°C)	260-340	300-360	360-400	370-390	400-420	410-450	380-400
T _g (°C)	150-220	170	230-380	160-295	250-270	300-400	170-340
G IC (J/m ²)	54-100	-	160-250	157-223	-	-	168
K IC (MPa m ^{1/2})	0.6	-	0.85	-	-	-	0/94

1.2 Piezoelectric Ceramic

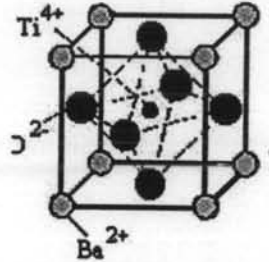


Figure 1.4 Perovskite structure of Barium Titanate.

The chemical formula for Barium Titanate is BaTiO_3 . As a powder it is white to grey in colour and has a perovskite structure (as in Figure 1.4). It is soluble in many acids including sulfuric, hydrochloric and hydrofluoric acids. It is insoluble in alkalis and water. In the pure form it is an electrical insulator. However, when doped with small amounts of metals, most notably scandium, yttrium, neodymium, samarium etc. it becomes semiconducting.

As a semiconductor it exhibits positive temperature of co-efficient of resistivity (PTCR) properties in polycrystalline form. This means at a certain temperature, called the curie temperature, the material will exhibit an increase in resistivity, the increase typically being several orders of magnitude. The Curie temperature can, to some extent, be controlled by the dopant. At the Curie temperature, barium titanate undergoes a phase change from tetrahedral to cubic, It has also been reported that single crystals of barium titanate exhibit negative temperature co-efficient of resistivity (NTCR) properties. Barium titanate also exhibits ferroelectric properties and is an excellent photorefractive material.

<u>Key Properties</u>	<u>Value</u>
Density (G.cm^{-3})	6.02
Melting Point ($^{\circ}\text{C}$)	1650
Young's Modulus (GPa)	67
Hardness (Mohr)	5 (http://www.azom.com)

The composition of most commercial high dielectric constant ceramic materials used for disk or multilayer capacitors are based on BaTiO_3 , because it displays the three dielectric anomalies associated with the three phase transitions at -90°C , 0°C , and 130°C , and these dielectric anomalies accompany high dielectric constants around the phase transition temperatures (Park, Y., et al, 1996). The dielectric constant of the conventional BaTiO_3 materials strongly depends on the grain sizes. When increased grain size, the orthorhombic-tetragonal phase transition temperature largely shifted towards higher temperature and the tetragonal-cubic phase transition temperature shifted toward lower temperature (Li, X., et al, 1997).

The BaTiO_3 based materials have wide potential applications, they are commonly used for making a number of electric devices like transducers, piezoelectric actuators, thermal switches, passive memory storage devices, etc. (Viswanath, R.N., and Ramasamy, S., 1997).

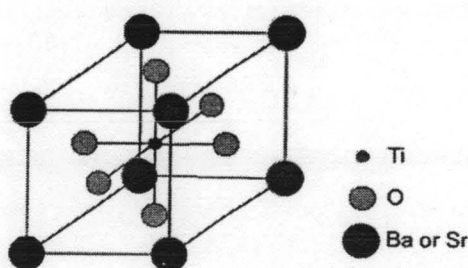


Figure 1.5 Structure of Barium Strontium Titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST).

As a high dielectric constant material, the curie temperature (T_c) of $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ (Figure 1.5) can be tailored easily by adjusting the ratio of Ba to Sr. It is known that the solid solution system is in a ferroelectric phase when Ba content is in the range

0.7-1.0, and in a paraelectric phase when Ba content is less than 0.7 at room temperature (Ding, X. et al, 2003). $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ is the solid solution of BaTiO_3 and SrTiO_3 , 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, 2001). The dielectric constant of barium strontium titanate, $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$, can be varied by an applied direct current electric field (Jiwei, Z. et al, 2002).

The sol-gel (Figure 1.6) process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials (<http://www.chemat.com/html/solgel.html>). Ceramic powder is a necessary ingredient for most of the structural ceramics, electronic ceramics, ceramic coatings, and chemical processing and environmental related ceramics.

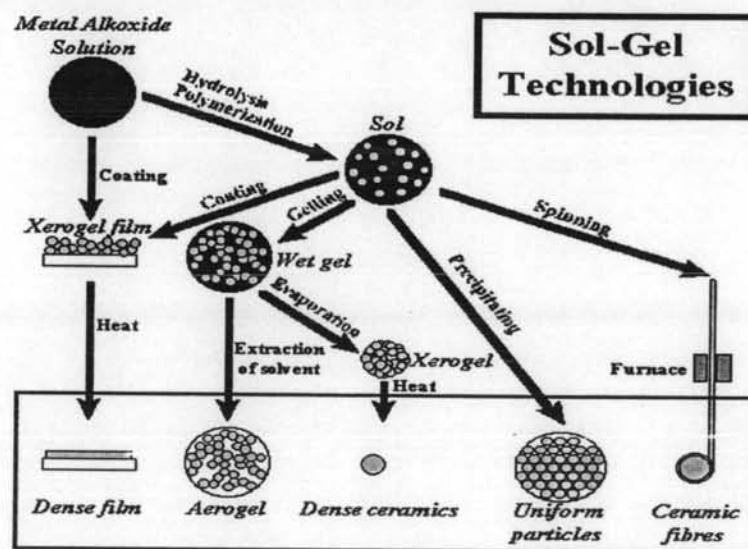


Figure 1.6 Overview of sol-gel process.

1.3 Piezoelectric Polymer Composite

In modern usage, composite materials are made from a filler, either particles, flakes or fibers, embedded in a matrix made of polymer, metal or glass. Combining a piezoelectric ceramic and a polymer host to form a flexible ferroelectric composite has been pursued in recent years in view of the greater flexibility allowed by these materials to suit particular properties such as mechanical, electrical, thermal and/or a coupling between these properties. Composite can be viewed as intermediate materials between these two extremes combining such attributes as flexibility and formability, to a whole range of piezoelectric and pyroelectric properties which themselves depend both on the ceramic-polymer mixture and on the processing employed in its manufacture.

The most commonly studied composites are the 0-3 and 1-3 configurations, although for different reasons. The 0-3 connectivity owes its popularity to the easy fabrication procedure which allows for mass production at a relatively low cost. The preparation of 0-3 ceramic polymer composite involves proper consideration regarding the materials to be used. The ceramic has to be transformed into a powder form from its usual block shape obtained after pressing, firing and sintering stages. A more recent approach for producing ceramic powders uses the sol-gel route where a very fine particle grain size is obtained through the direct calcinations of the gel powders. (Dias, C.J., and Das-Gupta, D.K., 1996)

Piezoelectric composites represent one of the latest technologies developed for engineering the last bit of high performance from a piezoelectric transducer. Moreover, a ceramic-polymer composites offers distinct advantages, such as a wide range of acoustic impedance matching, broad bandwidth, low electrical losses, and, for medical ultrasound applications, send-receive capability in a compact package. Considerable engineering ingenuity has been demonstrated in designing, fabricating, and packing the many types of diphasic structures. Major applications include hydrophones, sensors, and medical ultrasonics (Gene, H., 1999).