CHAPTER II
LITERATURE REVIEW

2.1 Polybenzoxazine

Polybenzoxazine-type phenolic resins are promising and interesting novel alternatives to traditional phenolic resins, which have many disadvantages (Takeichi *et al.*, 2005). Polybenzoxazines possess typical properties of traditional phenolic resins, such as heat resistance, good electrical properties, high mechanical properties, and excellent flame retardancy etc. Additionally, the molecular design flexibility of polybenzoxazines allows the properties of the cured materials to be tailored for a wide range of applications (Ardhyananta *et al.*, 2008). Therefore, polybenzoxazines have excellent properties that are not found in traditional phenolic resins as follow:

- Near zero volumetric change upon polymerization
- Low water absorption
- T_g much higher than curing temperature
- Fast mechanical property build-up as a function of degree of polymerization
- High char-yield
- Low Coefficient Thermal Expansion(CTE)
- Low viscosity
- Excellent electrical properties

Table 2.1 Comparative properties of various high performance polymers

Property	Epoxy	Phenolics	Toughened BMI	Bisox–phen (40:60)	Cyanate ester	P–T resin	PBZ
Density (g/cc)	1.2–1.25	1.24–1.3	2 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 7	0–130	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 (8C)	RT–180	150–190	220–300	175–225	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
Tg (°C)	150–220	170	230–380	160–295	250–270	300–400	170–340
GIC (J/m^2)	54–100	–	160–250	157–223	–	–	168
KIC (MPa m$^{1/2}$)	0.6	–	0.85	–	–	–	0/94

(Reghunadhan Nair,2004)

2.1.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

Typical benzoxazine monomers are easily prepared from phenol, primary amine and formaldehyde. Benzoxazine polymerizes via a thermally induced ring-opening reaction to form a phelic structure characterized by a Mannich base bridge (-CH$_2$-NR-CH$_2$-) as shown in scheme 2.1, without the need of harsh catalysts and no release of by-product or volatiles. Various types of raw materials, phenols, and amines with different substitution groups attached which provide additional polymerizable sites can also affect the curing process. Consequently, polymeric materials with desired properties may be obtained by tailoring the benzoxazine monomers.
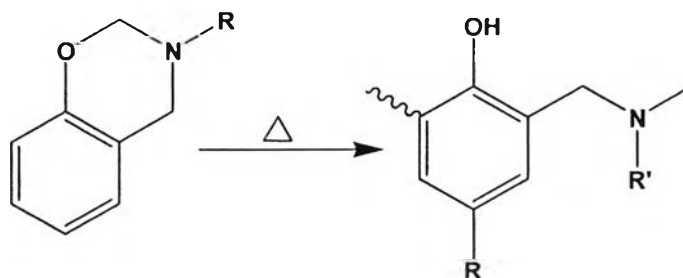
Scheme 2.1 Benzoxazine polymerization

2.1.1.1 Mono-functional Benzoxazine Monomer

Holly and.Cope (1944) first reported the condensation reaction of primary amines with formaldehyde and substituted phenol for the synthesis of well-defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent via two-step process. Later, it has been demonstrated that the preferred reaction site is the position ortho to the hydroxyl functionality on the aromatic ring (Burk *et al.*, 1965). The synthesis procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring (Burke *et al.*, 1965).

2.1.1.2 Di-functional and Multifunctional Benzoxazine Monomer

As a polymeric material, benzoxazines have traditionally been limited to low molecular weight oligomers. To overcome this limitation, Ishida and coworker (Ning *et al.*,1994) have developed a new class of difunctional or multifunctional benzoxazine monomers. The phenolic materials were obtained through thermally activated ring opening polymerization. The precursor was synthesized using bisphenol-A, formaldehyde and methyl amine in different solvents and referred to as BA-m, as a reference to two of its original ingredients: bisphenol-A and methylamine. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol-A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine ring and free phenol structures as shown in Figure 2.2

2.1.1.3 High Molecular Weight Polybenzoxazine

High molecular weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone were prepared from bisphenol-A, various diamines, and paraformaldehyde. Partially ring-opened structure was observed, but the ratio of the ring-closed structure in the precursor was high enough to be used as polybenzoxazine precursors (Takeichi *et al.*, 2005). Several methods were applied to prepared high molecular weight benzoxazines. By using the solventless technique, it was found that when reactants were mixed without a solvent an insoluble solid

mass was obtained. Therefore, the solvent method was applied. generally, the forma-
tion of soluble oligomers. The nonpolar solvent systems are used for the synthesis of
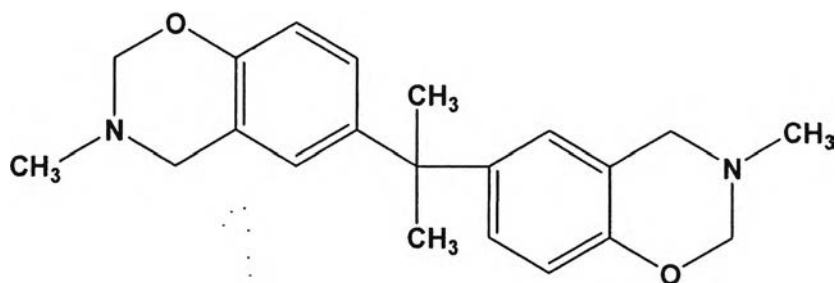high yields with high-purity benzoxazine monomer (Ishida *et al.*, 1998)

Figure 2.2 Chemical structure of Bisphenol-A and methylamine based benzoxazine
monomer.

2.2 Carbon Aerogel

Carbon aerogels are synthesized by the polycondensation reaction of differ-
ent organic monomer such as phenol-furfural (Wu *et al.*, 2005), melamine-
formaldehyde system (Zhang *et al.*, 2003), but are mostly produced by resorcinol
and formaldehyde in different solvent and using different catalysts through a sol-gel
transition, discovered by Pekala et al. at the beginning of the 1990s (Pekala *et al.*,
1989). Because of their unique microstructures consisting of carbon nano-particles
and nano-pores, Carbon aerogels have been applied in many fields, such as wastewa-
ter treatment (Hrubesh *et al.*, 2001), supercapacitors (Zhu *et al.*, 2006), advance cata-
lyst supports (Mereno-Castilla *et al.*, 2005), etc.

2.2.1 Synthesis of the Carbon Aerogel

There are three main stages in the preparation of carbon aero-
gels. The first is the preparation of solvent system, its gelation, and the subse-
quent curing of the gel. The second stage is the drying of the sol-gel. During
the conventional evaporation process of the solvent, a liquid-vapor meniscus is
formed due to the surface tension of the liquid, and leads to a collapse of the
pore structure. To avoid this problem, practically a CO_2 supercritical drying

technique is applied. Supercritically dried gels are called aerogel. And the third stage is the pyrolysis of the dried gel in flowing N_2 or Ar at temperature between 700 and 1000°C. During this procedure, the organic aerogels transform to a carbon network. Activation of the aerogel can be carried out by its gasification with steam or CO_2. This treatment increases the micro- and meso-pore volumes. Figure 2.2-2.4 show the porous structure of carbon aerogel which were produced by resorcinol and formaldehyde with differnet resorcinol and formaldehyde ratio.The resorcinol and formaldehyde ratio provides controlling the partical size from manometer up to microscale.
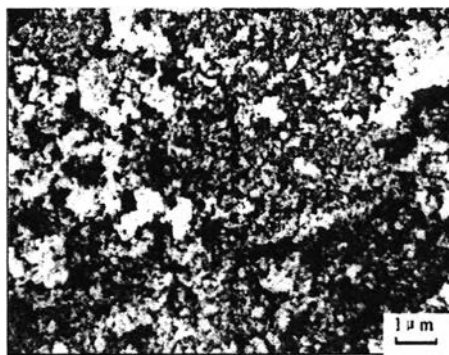

Figure 2.2 SEM of carbon aerogel with RC ratio 500 and RF mass concentation 30% (Shen *et al.*, 2004).
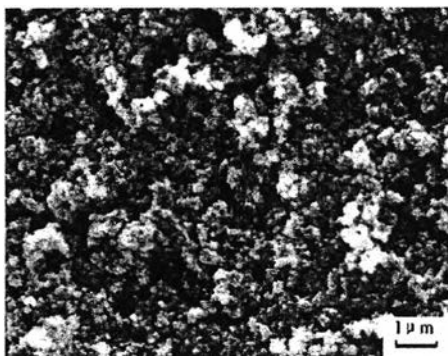

Figure 2.3 SEM of carbon aerogel with RC ratio 1000 and RF mass concentration 30% (Shen *et al.*, 2004).
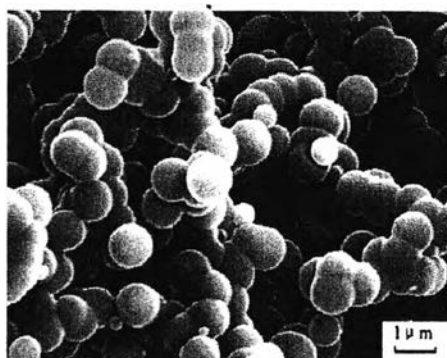
Figure 2.4 SEM of carbon aerogel with RC ratio 1500 and RF mass concentration 30% (Shen *et al.*, 2004).

2.3. Porous Materials

The classification of pores according to size has been a discussed for many years, but in the past, the terms "micropore" and "macropore" have been applied in different ways by physical chemists and some other scientist. With an attempt to clarify this situation, the limits of size of the different categories of pores included in Table 3.1 have been proposed by the International Union of Pure and Applied Chemistry (IUPAC) (Isizaki et al.,1988 and Rouqueol et al,.1999). As indicated, the "pore size" is generally specified as the "pore width", i.e. the available distance the two opposite walls. Obviously, pore size has a precise meaning when the geometrical shape id well defined. Nevertheless, for most purposes, the limiting size is that of the smallest dimension, and this is generally taken to represent the effective pore size. Micropores and mesopores are especially important in the context of adsorption.

Table 2.2 Definitions about porous solids

Term	Definition
Porous solid	Solid with cavities or channels which are deeper than they are wide
Micropore	Pore of internal width less than 2 nm
Mesopore	Pore of internal width between 2 and 50 nm
Macropore	Pore of internal width greater than 50 nm
Pore size	Pore width (diameter of cylindrical pore or distance between opposite walls of slit)
Pore volume	Volume of pores determined by stated method
Surface area	Extent of total surface area determined by given method under stated conditions

According to the IUPAC classification, porous materials are regularly organized into three categories on a basis of predominant pore size as follows:

- Microporous materials (pore size <2 nm) include amorphous silica and inorganic gel to crystalline materials, such as zeolites, aluminophosphates, gallophosphates, and related materials.

- Mesoporous materials (2 nm $\leq$ pore size $\geq$ 50 nm) include the M41S family (e.g. MCM-41, MCM-48, MCM-50, and etc.) and other non-silica materials synthesized via intercalation of layered materials, such as double hydroxides, metal (titanium, zirconium) phosphates, and clays.

- Macroporous materials (pore size > 50 nm) include glass-related materials, aerogels, and xerogels.

Nowadays, micro- and mesoporous materials are generally called "nanoporous materials". Particularly, mesoporous materials are remarkably very

suitable for catalysis applications, whereas the pores of microporous materials may become easily plugged during catalyst preparation is high loading is sought.

2.4. Gas sensor

There are two main classes in gas-sensing materials: inorganic metal oxide semiconductor i.e., SnO_2, WO_3, etc. (Shimizu *et al.*, 1999) and polymer-based material including conductive polymers (Miasik *et al.*, 1986) and conductive polymer composites (Zhang *et al.*, 2005). In this section, only conductive polymer composites are discussed.

Conductive polymer composites have been widely utilized to make gas sensors, for they are easy to process and low cost. General polymers are insulator; therefore, to make conductive polymer composites, conductive fillers are added. The sensing mechanism of these sensors described by the so-called percolation theory as follows (Dong *et al.*,2003). The filler particles are connected with each other forming chain-like conductive paths in the matrix. Sorption of organic vapors in to the polymeric phase of the composites leads to swelling of the matrix, expands the inter-particulates' interval and partially destroys the conductive networks. As a result, a drastic rise in resistivity of the material is perceived.

1. Gas-sensitive composites from multi-walled carbon nanotubes/
   polystyrene

Zhang *et al.* (2008) developed the promising candidates for gas sensors to detect, distinguish and quantity organic vapors by conductive polymer composites of styrene (PS) in a presence of multi-walled carbon nanotubes (MWCNTs). The thickness of composite films are 10-20 μm. In case of insitu polymerization, the low-molecular-weight monomers are able to penetrate into the aggregated MWCNTs and result in better dispersion of the fillers in the subsequent polymerization. The fillers are uniformly dispersed in the matrix, leading to lowing percolation threshold of about 4 wt%. The composites synthesized through polymerization-filling possess different sensitivities to different vapors, indicating that the composites might be used to distinguish different organic vapors. On the whole, the composites show high responsibility to the good solvents of PS, like THF, benzene, toluene, cyclohexane,

carbontetrachloride, chloroform, ethyl acetate and diethyl ether, but low response to the non-solvent, such as alcohol..

    2. Poly(4-vinylpyridine)/carbon black composite as a humidity sensor

Li *et al.* (2007) developed the resistive-type polymeric humidity sensors by using poly(4-vinylpyridine) grafted onto carbon black to obtain a composite, which was further quaternized and crosslinked with bromobutane and 1,4-dibromobutane. Introducing carbon black into the polymer matrix can increase the conductivity of the resistive-type polymeric humidity sensors in dry atmosphere, and thus make the measurement of low humidity possible. Poly(4-vinylpyridine) was simultaneously quaternized and crosslinked with 1,4-dibromobutane to form a network structure, which not only introduced ions into the composite and increased the water adsorption ability, but also greatly improved the stability of the composite to humidity. The best response was obtained for the composite with a feeding ratio of carbon black to poly(4-vinylpyridine) of 1:9 and a crosslinking reaction time of 6 h. The composite can be used range of 0-97%RH.

    3. Novel gas and contamination sensor materials from polyamide-block-poly(ethylene oxide)-grafted carbon black

Iwata *et al.* (2006) reported the sensor materials which could detect vapors and contamination in solution by grafting of polyamide-block-poly(ethylene oxide) (PA-b-PEO) onto a carbon black surface by γ-ray radiation grafting. The hydrophilicity was controlled by changing the content of the PEO block. The higher content of PEO showed the higher hydrophilicity. The percentage of PA-b-PEO grafting was determined to be 3.4-6.6%. They found the results as following.

    1. PA-b-PEO (PEO 21, 39 mol%) with higher hydrophilic PEO block content show a higher sensitivity to hydrophilic water and a lower sensitivity to hydrophobic n-hexane on the other hand PA-b-PEO (PEO 3, 7 mol%) with lower PEO block content show hydrophobic nature and the sensitivity is excellent to hydrophobic n-hexane but not to hydrophobic water.

    2. he electric resistance of the composite from PA-b-PEO (PEO 21, 30 mol%) with a higher hydrophilic PEO content drastically increased when it was dipped in n-hexane solution containing contamination, and returned to initial resistance when it was transferred to dry n-hexane.

3. The electric resistance of the composites from PA-b-PEO (PEO 3, 7 mol%) with a lower hydrophilic PEO content drastically increased when it was dipped in aqueous solution containing contamination, and returned to initial resistance when it was transferred to pure water.

4. Carbon / polystyrene composite as candidtes for gas sensing materails.

Li *et al.* (2003) reported polymer-based composites consisting of polystyrene and carbon black for gas sensing materials. The composite was prepared by in-situ polymerization of styrene in presence of carbon black.The thickness of composite about 0.08~0.12 mm. The response of gas sensing material were high to the vapors of non-polar and low polar solvents, and low response to high polar solvent vapors as well. Not only conductivity of the composites which influences on the gas sensitivity of composite but also the absorption characteristics of both the matrix and the fillers. Therefor, composites's performace can be tailored by controling filler content, molecular weight and molecular weight distribution of matrix polymer, etc.