



CHAPTER II

LITERATURE REVIEW

2.1 Polybenzoxazine

A series of polybenzoxazines (PBZ) obtained by the ring-opening polymerization of cyclic monomers, benzoxazines, has been developing as a novel type of phenolic resin. The monomers are easily prepared from phenols, amines and formaldehyde. The wide variations of raw materials, phenols and amines, allow considerable molecular-design flexibility for the cyclic monomers. Polybenzoxazines provide characteristics found in the traditional phenolic resins such as high heat resistance and flame retardance. They also provide characteristics that are not found in the traditional phenolic resins such as excellent dimensional stability, low water absorption and good dielectric properties (Reiss G *et al.*, 1985).

2.1.1 Features of Polybenzoxazines

These new materials, belonging to the addition 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 (Ishida H., 1998). Polybenzoxazines overcome several shortcomings of conventional novolac and resole-type phenolic resins, while retaining their benefits. PBZ resins are expected to replace traditional phenolics, polyesters, vinyl esters, epoxies, Bismaleimides (BMI), cyanate esters and polyimides in many aspects. The molecular structure of PBZ offers superb design flexibility that allows properties of the cured material to be controlled for specific requirements of a wide variety of applications. The physical and mechanical properties of these new polybenzoxazines are shown to compare very favorably with those of conventional phenolic and epoxy resins. The properties of PBZ compared with various high performance polymers are summarized in Table 2.1. The resin permits development of new applications by utilizing some of their unique features such as (Ishida H *et al.*, 1995):

- 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 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	1.24–1.32	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	0.3/0.5	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	0.2/0.4	2	2.3–2.9
Dielectric constant (1 MHz)	3.8–4.5	0.4/10	3.4–3.7	–	2.7–3.0	3.1	3–3.5
Cure temperature (°C)	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
T_g (°C)	150–220	170	230–380	160–295	250–270	300–400	170–340
G_{IC} (J/m ²)	54–160	–	160–250	157–223	–	–	168
K_{IC} (MPa m ^{1/2})	0.6	–	0.85	–	–	–	0.94

2.1.2 Structure–Property Relationship

Ishida *et al.* (1998) reported that the physical, mechanical and thermal properties of polybenzoxazines are primarily determined by the nature of the diphenol and amine used as reactants. The system derived from 4,4-dihydroxybenzophenone and aniline provides a combination of high thermal stability (5% weight loss at > 400 °C) and high T_g (340 °C). In this case, the thermal stability for dihydroxybenzophenone-based benzoxazine was achieved at the cost of mechanical performance. To improve the impact property, PBZ derived from aliphatic amine was preferred.

Table 2.2 Structure-property relationship of polybenzoxazines

Properties	Bis benzoxazine formed from		
	BPA – methyl amine	BPA – aniline	Dihydroxy benzophenone – aniline
Tensile strength (MPa)	103	126	6.2
Tensile modulus (GPa)	3.8	4.5	>6
Strain at break (%)	2.6	2.9	2.3
Impact strength (J/m)	31	18	-
Polymer density	1.122	1.195	1.250
T_g (°C)	180	170	340

2.1.3 Chemical Methodologies for Synthesis of Benzoxazine Monomers

2.1.3.1 *Mono-functional Benzoxazine Monomers*

Holly and Cope (1944) first reported the condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two-steps. Later, Burke found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge (Burke W.J., 1949). The synthetic 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 WJ *et al.*, 1965).

2.1.3.2 *Di-functional and Multifunctional Benzoxazine Monomers*

Ishida and coworkers (Ning X, Ishida H., 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 BAm, 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 rings and free phenol structures as shown in Figure 2.1.

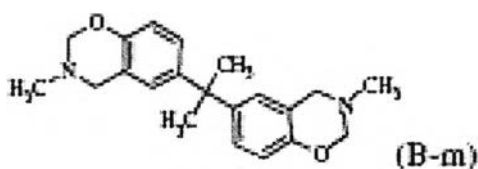


Figure 2.1 Chemical structure of Bisphenol-A and methylamine based benzoxazine monomer.

2.1.4 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. The first method attempted used the solventless technique, they found that when reactants were mixed without a solvent, an insoluble solid mass was obtained. Therefore, the solvent method was applied. Generally, the formation of a typical cyclic benzoxazines is usually accompanied by ring opening and the formation of soluble oligomers. The nonpolar solvent systems are used for the synthesis of high yields with high-purity benzoxazine monomer (Ishida *et al.*, 1998).

2.2 Carbon aerogels

Due to the continuing increase in the cost of fuels and global environmental concerns, the development and specification of materials for alternative energy is very attractive. The carbon aerogel is a nanoporous material with an open porosity and a good electrical conductivity. The morphology of carbon aerogels can be modified as a function of different synthesis parameters. This characteristic makes the carbon aerogel particularly well adapted for various applications varying from electrodes (supercapacitors, fuel cells) to a host material.

Aerogels are unique porous materials with a continuous three-dimension framework whose composition, structure and properties can be controlled at the nanometer scale. Aerogels resulting from the reaction of resorcinol with formaldehyde have been investigated in great detail (Tamon *et al.*, 1998). Moreover these materials can be pyrolyzed in an inert atmosphere to form carbon aerogels (Pekala R.W., 1989).

2.2.1 Carbon Aerogel Synthesis

The elaboration of carbon aerogels is done in different steps.

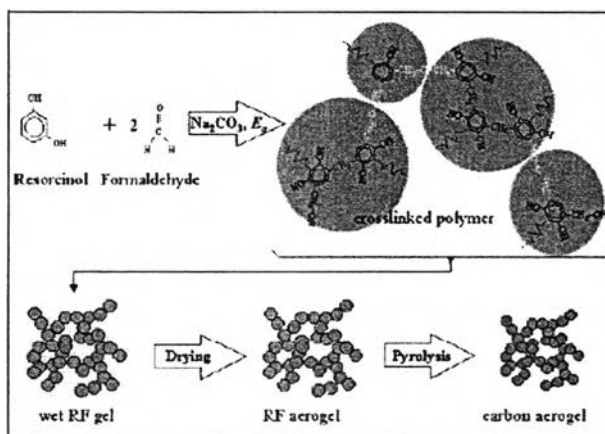


Figure 2.2 The overall process for the formation of the carbon aerogel (Achard P., 2003).

2.2.2 Structure and Properties of Carbon Aerogels

Carbon aerogels, which are highly porous materials consisting of a continuous rigid solid framework and an open, continuous network of pores, represent attractive properties such as:

- A high electrical conductivity (25-100 S/cm)
- Controllable pore structure
- Highly useable surface area (up to 1100 m²/g)
- Biocompatibility
- Anti-carrion by acid or base etc.

Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR), N₂ adsorption, Small-angle X-ray scattering (SAXS), Mechanical testing, Electrochemical testing etc. have been used to characterize organic and carbon aerogels especially, the analysis of mesoporous and microporous structures of the aerogels is very important for their applications.

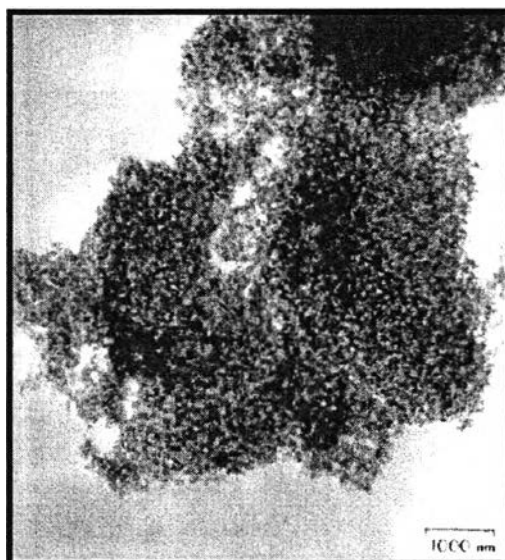


Figure 2.3 Transmission Electronic Microscopic (TEM) of the carbon aerogel.

2.2.3 Carbon Aerogel Application

The organic aerogels (before pyrolysis) can be used as thermal and phonic insulators. The carbon aerogels can serve as support of catalytic active phases as platinum or the ruthenium to be used as electrode materials having a big active surface in the case of the supercapacitors (Pekala R.W. *et al.*, 1998). They can also be considered as electrode materials to support catalysts in fuel cells (Ye S. *et al.*, 1997) for the deionisation of the solutions (Farmer J.C. *et al.*, 1996). Furthermore, they can also act as a material host for gas storage (Langohr D. *et al.*, 2002).

2.2.4 Carbon Aerogels Prepared by Using Catalysts

Most carbon aerogels are obtained by basic catalyst, mainly using alkaline carbonates (Kong F.M. *et al.*, 1993). However, different acid catalysts have also been used to prepare these materials, including perchloric acid dissolved in acetone (Barbieri O. *et al.*, 2001), nitric acid (Merzbacher C.I. *et al.*, 2001), and acetic acid (Brandt R. *et al.*, 2003). The main difference when perchloric acid instead of Na_2CO_3 dissolved in water is used as catalyst (Barbieri O. *et al.*, 2001) is the aggregation of primary particles of the aerogels. This derives from the different gelation mechanism in each sample series. The use of nitric acid as catalyst (Merzbacher C.I. *et al.*, 2001) gives rise to a carbon aerogel with a very low density (0.18 g/cm^3). Almost all structural properties of carbon aerogels derived from base-catalyzed resorcinol-formaldehyde aerogels were reproduced using different acetic acid concentrations as catalyst (Brandt R. *et al.*, 2003).

2.2.5 Characterization of the Microstructures of Carbon Aerogels

FT-IR spectroscopy in combination with TGA and low temperature nitrogen adsorption are used to determine the details of microstructure changes within the organic aerogel network upon pyrolysis, as well as transmission electron microscopy (TEM), which is used to characterize the morphology of the aerogels.

IR combined with TGA, TEM, and nitrogen adsorption are employed to study these changes in detail. Appreciable transformation of aerogel structure occurs during $250\text{--}600^\circ\text{C}$, which results from the release of water, organic groups and a simultaneous rearrangement of aromatic rings. A new band occurring at 874 cm^{-1} in IR spectra after 400°C is associated with the IR-active vibration states of graphitic structure. With the increase of pyrolysis temperature, the density, surface area and

total volume of aerogels keep increasing; on the contrary, the pore size distribution becomes narrower and the pore size decreases. The carbon aerogel microspheres are smaller than their organic aerogel precursors as a result of shrinkage during pyrolysis (Wen-Cui Li. *et al.*, 2000).

2.2.6 Control of Mesoporous Structure of Organic and Carbon Aerogels

Tamon H. *et al.* (1997) investigated the control of mesoporous structure of the aerogels by changing the amount of reactants, diluent and basic catalysts used in the polycondensation. The adsorption characteristics of ethane and ethylene on the aerogels were also discussed. The following conclusions were obtained.

(1) The mesopore radius of the sol-gel polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde, and prepared resorcinol-formaldehyde (RF) aerogel can be controlled in the range of 2.5–9.2 nm by changing the mole ratio of resorcinol to Na_2CO_3 used as catalyst (R/C) and the ratio of resorcinol to distilled water used as diluent (R/W).

(2) The mesopore radius of carbon aerogel can be controlled in the range of 2.0–6.1 nm by taking into account of the shrinkage of RF aerogels during pyrolysis.

(3) As the pyrolysis temperature increases, the mesopore volume becomes small but the peak radius of pore size distribution is kept.

(4) As the pyrolysis temperature increases, ethane adsorption becomes larger than ethylene adsorption on the aerogels. The carbon aerogels prepared by pyrolysis at 1000°C have the same adsorption characteristics of ethane and ethylene as activated carbons.

2.3 Porous Materials

The classification of pores according to size has been under discussion for many years, but in the past, the terms “micropore” and “macropore” have been applied in different ways by physical chemists and some other scientists. With an attempt to clarify this situation, the limits of size of the different categories of pores included in Table 2.3 have been proposed by the International Union of Pure and Applied Chemistry (IUPAC) (Ishizaki *et al.*, 1988 and Rouquerol *et al.*, 1999). As

indicated, the “pore size” is generally specified as the “pore width”, i.e. the available distance between the two opposite walls. Obviously, pore size has a precise meaning when the geometrical shape is 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 2.3 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 \leq 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 if high loading is sought.

2.4 Gas sensor

There are two main classes in gas-sensing materials: inorganic metal oxide semiconductors (MOS) i.e., SnO₂, WO₃, etc. (Shimizu Y. *et al.*, 1999) and polymer-based materials including conductive polymers (Miasik J.J. *et al.*, 1986) and carbon black–polymer composites (Lonergan M.C. *et al.*, 1996) for the chemoresistive sensors and insulating polymers, such as polysiloxanes (M. Haug *et al.*, 1993), for the surface acoustic wave or the quartz crystal microbalance devices. Generally, MOS devices operate at higher temperatures in the range of 200–500°C for detecting chemical vapors with desired sensitivity and selectivity, while the polymer-based chemical sensors run at lower temperatures below 100°C. The temperature of a sensing layer affects its baseline conductance, the quantity of adsorbed gases and the diffusion rates of analytes into the film, so that the vapor detection sensitivity strongly depends on the operation temperature. Therefore, the implementation of a temperature-controlled hotplate is very important in developing a reproducible sensor device.

2.4.1 Gas Sensor Arrays based on Polymer-Carbon Black

Haifen Xie *et al.*, (2004) developed a novel chemical gas sensor array composed of polymer-carbon black. Poly (4-vinyl phenol) (PVPH), poly (ethylene oxide) (PEO), polycaprolactone (PCL) mixed with carbon black 2000 are employed as the sensing materials which are immobilized on the array of the interdigitated microelectrode pairs. The resistance changes with the organic gases (acetone, ethanol, toluene, methanol, tetrahydrofuran) and their mixed gases at low concentration have been examined. By the pattern recognition analysis of the

responses of microsensors, five single gases and their mixed gases can be easily identified at the concentrations between 200 and 2000 ppm. The measurement data show that this configuration of interdigitated microelectrodes was a good choice to detect the low concentration of organic gases.

2.4.2 Chemical Sensors based on Polymer Composites

The electrically conductive polymer composites have been investigated for chemical sensors. Several commodity thermoplastic such as, HDPE, PS, PP, HDPE/PS and HDPE/PP blend was used as the matrices. Carbon black with particle in the range of 10-110 nm. Was selected as a filler. Electrical conductivity, mechanical strength, Vicat softening temperature and melt rheology were investigated. The lowest percolation threshold was achieved at 2 wt. % of carbon black, which resulted in electrical resistance of $10^7 \Omega \text{ m}$. Along with the filler volume the Vicat softening temperature increased at every polymer matrix for a few centigrades. At the highest filler content the tensile Young modulus of composites was four times higher, whereas elongation at break decreased substantially if compared to the net polymers. Melt viscosity increased with carbon black content, making composites hardly processable at high filler loadings (Kozłowski Marek *et al.*, 2005).

2.4.3 Detection of Chemical Warfare Agents using Nanostructured Metal oxide Sensors

The feasibility of thick-film chemical sensors based on various semiconductor metal oxides to reliably detect chemical warfare agents has been studied. Nanocrystalline semiconductor metal oxide (SMO) powders were used as initial materials for the sensor fabrication. The thick films were prepared using a simple drop-coating technique accompanied with in situ annealing of the deposited films by a heater that was integrated into the sensor's platform. The sensors were exposed to mixtures of hexane, diesel oil vapor, methanol, 1,5-dichloropentane (DCP), or dimethyl methylphosphonate (DMMP) with air. DCP and DMMP were considered as simulants of mustard gas and nerve agents, respectively. The performance of the sensors was investigated over a wide range of operating temperatures. They were additionally tested with mustard gas, sarin and soman at a certified live agent facility.

The study was particularly emphasized on the ability of an array of sensors to detect and identify agents in mixtures of interferences (Tomchenko A.A. *et al.*, 2004).