



## CHAPTER II

### LITERATURE REVIEW

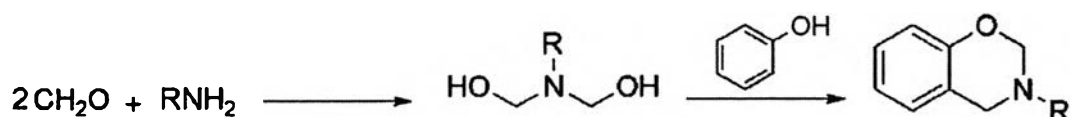
#### 2.1 Polybenzoxazine

Polybenzoxazines, as a novel type of phenolic resin, offer many advantages in comparison with the traditional phenolic resins. Their precursors can be easily prepared from inexpensive raw materials, and polymerized without using strong acid or basic catalysts and no by-product release. Polybenzoxazines also provide unique characteristics like such as low water absorption and high dimensional stability due to near-zero shrinkage upon curing (Ishida *et al.*, 1996). Therefore, they are widely applied in various fields such as protective coatings for electrical circuits and computer chips, structure and interior materials of airplane, curing agents for other synthetic resins, varnishes which form films with a good resistance to water, alkali, solvents. The major disadvantages of typical polybenzoxazines are their brittleness and high temperature needed for the polymerization. Various studies have been reported aiming at performance improvement of polybenzoxazines. Generally, for performance enhancement, the preparation of novel monomers, copolymers, polymer alloys, and fiber reinforced composites have become increasingly attractive to overcome the shortcomings of the typical polybenzoxazines

##### 2.1.1 Chemical Methodologies for Synthesis of Benzoxazine Monomer

Benzoxazine monomers are typically synthesized by using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution (Ning *et al.*, 1994) or solventless methods (Ishida Pat. 5,543,516, 1996). Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached. These substituting groups can provide additional polymerizable sites and also affect the curing process. Consequently, polymeric materials with desired properties may be obtained by tailoring the benzoxazine monomer. In this section synthesis of different benzoxazine monomers is discussed.

Holly *et al.* (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 (1949) found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge. In 1965, the same group synthesized Mannich condensation of benzoxazine in a solvent by addition of amine to formaldehyde at lower temperatures to form an N,N-dihydroxymethylamine derivative at first, which then reacted with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring (Figure 2.1).



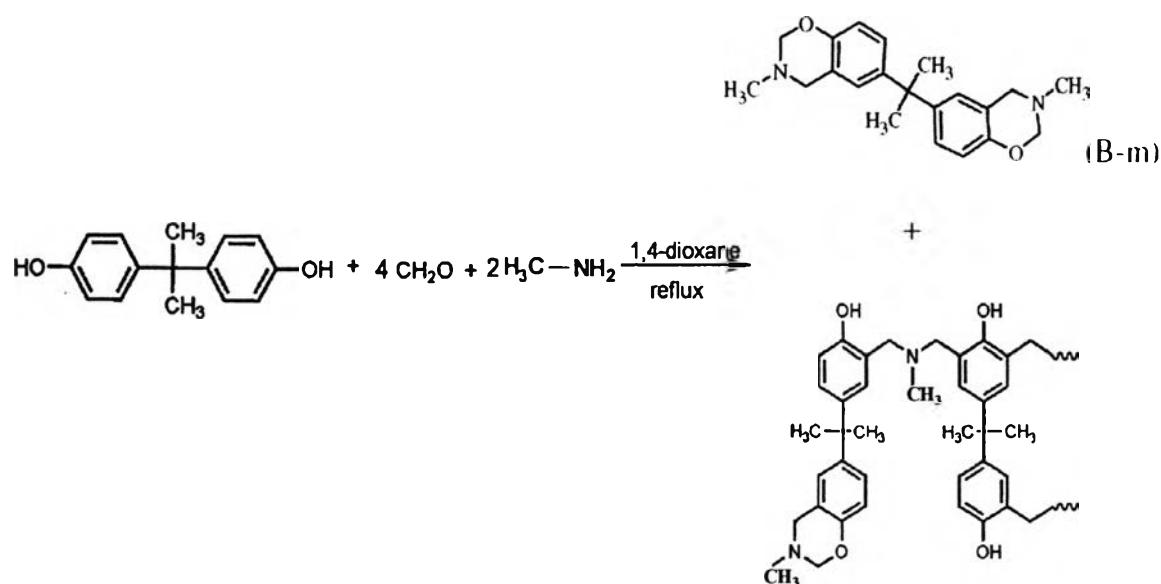
**Figure 2.1** Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, Ishida *et al.* (1996) developed a solventless synthesis in the melt state.

The reaction mechanism and kinetics of this solventless synthesis were proposed by Liu (1995). In a typical solventless synthesis, the reactants, i.e., aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. It should be pointed out that formaldehyde is not typically used as it evaporates easily and causes stoichiometric imbalance. Instead, paraformaldehyde is used. The choice

for phenols and amines provides the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless synthetic method are the improvement of reaction times compared with the traditional synthetic route and the formation of fewer intermediates and by-products that are contaminants.

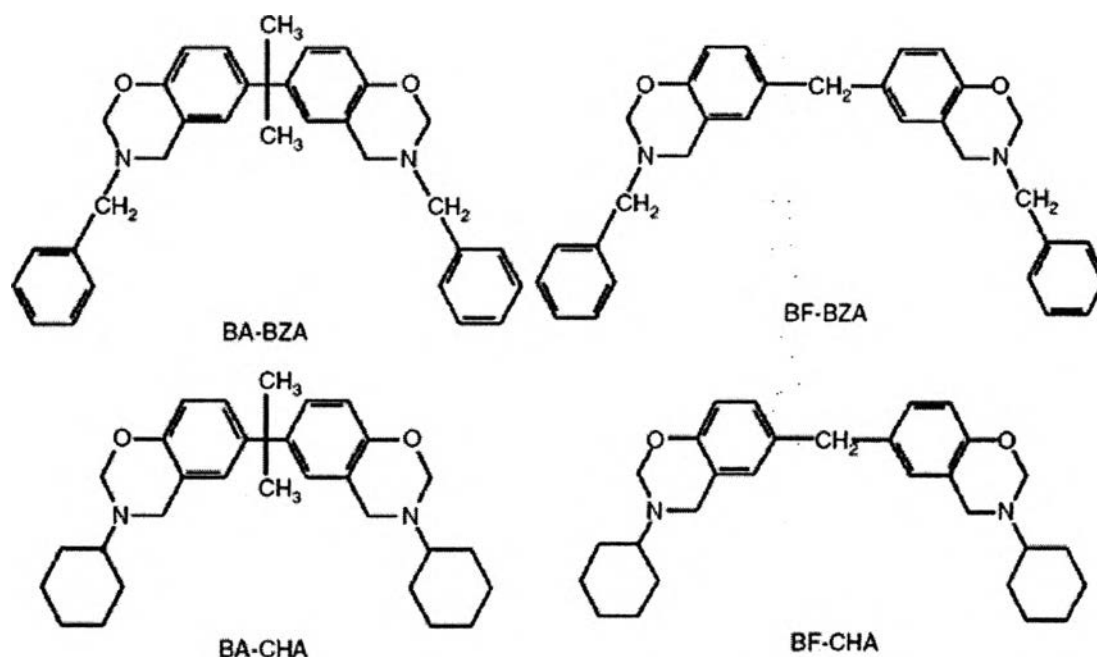
Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with an average molecular weight around 1000 Da. Thus, no materials could be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high-molecular weight linear structures were unobtainable (Riess *et al.*, 1985). To overcome this limitation, Ning *et al.*(1994) have developed a new class of difunctional or multifunctional benzoxazine monomers which undergo thermally activated ring opening polymerization to form phenolic materials. The precursor was synthesized using bisphenol-A, formaldehyde and methyl amine in different solvents and referred to as B-m (Figure 2.2), 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 detected by NMR, FTIR and SEC. It was observed that the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility.



**Figure 2.2** Synthesis of bisphenol-A and methyl amine based benzoxazine (B-m) monomer.

Garea *et al.* (2006) synthesized four different benzoxazine monomers bis(4-benzyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BA-BZA), bis(4-cyclohexyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BA-CHA), bis(4-benzyl-3,4-dihydro-2H-1,3-benzoxazinyl) methane (BF-BZA), bis(4-cyclohexyl-3,4-dihydro-2H-1,3-benzoxazinyl) methane (BF-CHA) led to products (Figure 2.3), which include oligomers revealed by  $^1\text{H-NMR}$  and GPC. The quantity of oligomers mainly depends on the basicity of the oxygen and nitrogen atoms from the oxazine rings, which influences the possibility of oxazine rings opening and, thus, the formation of oligomers. Therefore, the benzoxazine monomers obtained from bisphenol-A (BA) exhibit a higher concentration of oligomers than those based on bisphenol-F (BF). The effective thermal polymerization of the benzoxazine monomers may be followed by GPC, which shows that there are two main factors which influence the polymerization reaction: the basicity of the N and O atoms from the oxazine rings and the oligomers already exist in the monomers from their synthesis, which may act as a catalyst through the phenolic groups. FTIR proved the gradual formation of the tetrasubstituted aromatic rings within the polymer, the process depending on time and, again, on the initial concentration of the oligomers in the monomers. The  $T_g$  values of the obtained polybenzoxazines, as determined from

tan  $\delta$ -temperature curves, depend mainly on the nature of the phenolic component and less on the amine component. The dependence of ionic conductivity against time during the polymerization of the benzoxazine monomers gives the value for the gel time and, therefore, the reactivity of each of the benzoxazine monomers. The main difference in the reactivities for monomers based on BA and BF is due to the initial concentration of oligomers in each monomer, while the minor difference in the reactivities of the monomers based on the same phenol but with different amines is explained in terms of the electrondensity at the nitrogen atom from amine.

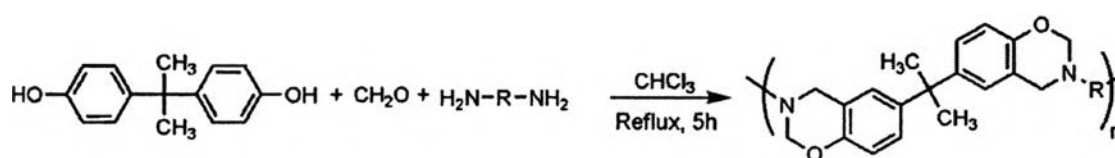


**Figure 2.3** Chemical structures of the synthesized benzoxazine monomers.

### 2.1.2 Preparation of High Molecular Weight Benzoxazine Precursors

Preparation of high molecular weight benzoxazine precursors would result in gel or insoluble solid because of the ring-opening polymerization of the once-formed cyclic ring. If it is possible to obtain soluble high molecular weight polybenzoxazine precursors, processing into thin films should become very easy, and application into the fields for which the low molecular weight cyclic monomer has not been used will be realized.

High molecular weight oligomeric benzoxazine precursors have been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde (Figure 2.4). The precursors were obtained as soluble white powder. The structure of the precursors was confirmed by IR, <sup>1</sup>H-NMR and elemental analysis, indicating the presence of cyclic benzoxazine structure. The precursor solution was cast on a glass plate, giving transparent and self-standing precursor films, which were thermally cured up to 240 °C to give brown transparent polybenzoxazine films. The toughness of the crosslinked polybenzoxazine films from the high-molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass-transition temperature of the polybenzoxazines derived from the high-molecular weight oligomeric precursors were as high as 238–260 °C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability (Takeichi et al., 2005).



**Figure 2.4** Synthesis of oligomeric benzoxazine precursors.

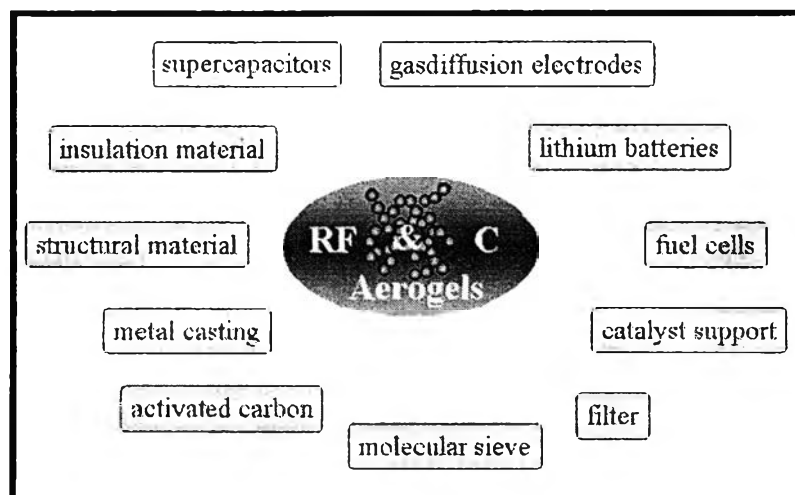
Agag *et al.* (2006) prepared polybenzoxazine matrix through high molecular weight polybenzoxazine precursors. They have used AB-type aminophenols instead of amines and phenols separately, the self-standing thin films from the precursors were obtained before curing by casting the precursor solutions onto glass plates. After the thermal treatment of the AB polybenzoxazine precursor films up to 250 °C, reddish-brown, transparent polybenzoxazines have been obtained. Both viscoelastic analyses and TGA have indicated that the thermosets

derived from these novel AB precursors have excellent thermomechanical properties as well as high thermal stability. This enhancement in the thermal properties can be attributed to the increase in the crosslinking density and hence suggests that the use of AB precursors is an effective approach for obtaining a novel polybenzoxazine matrix with excellent thermomechanical properties.

Polybenzoxazines is the novel thermoset that can be obtained by the ring-opening polymerization, and possess various advantageous characteristics that are not found in the traditional phenolic resins. Polybenzoxazine also possess characteristics as benign to its surroundings as flame-retardant properties and does not produce any harmful volatiles. In recent studies on the development of polybenzoxazine as a novel type of phenolic resin were reviewed. The designing of novel monomers and high molecular weight precursors are a promising approach to prepare any type of polybenzoxazines by taking advantage of the wide selection of mono- and diamines and also mono- and bisphenols. Development of basic studies and application into various fields are expected.

## **2.2 Carbon aerogels**

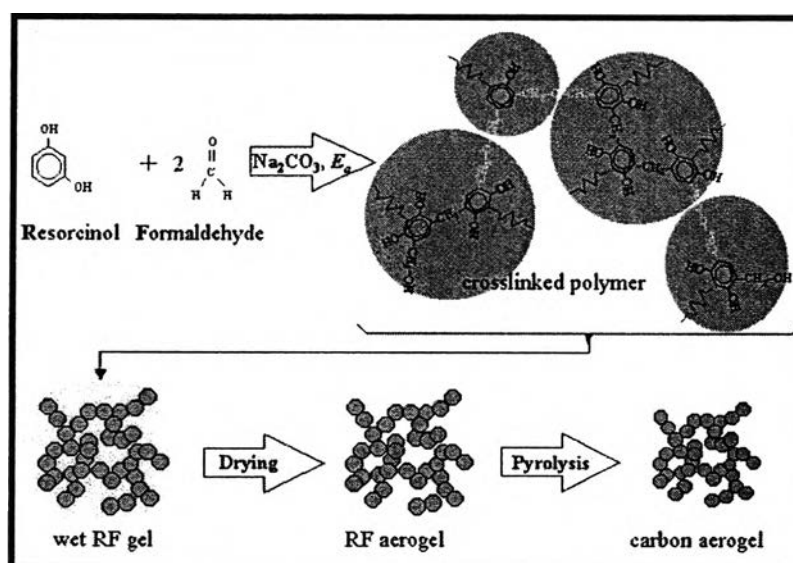
Carbon aerogels, discovered by Pekala *et al.*(1989), compose of particles with sizes in the nanometer range, covalently bonded together. They are highly porous materials consisting of a continuous rigid solid framework. Carbon aerogels can be uses in many applications such as gas adsorption devices, for heavy metals and ionsremoval, purification of drinking water, electronic capacitors, fuel cell electrodes, parts for inertial confinement fusion targets, catalyst support and chromatographic packing.



**Figure 2.5** General application of carbon aerogels.

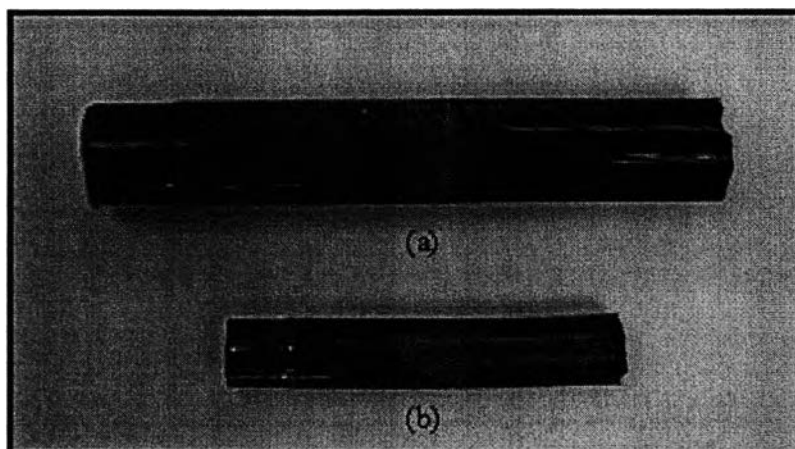
### 2.2.1 Preparation of Carbon Aerogels

Carbon aerogels have been generally synthesized from resorcinol-formaldehyde, phenol resorcinol-formaldehyde (Pekala et al., 1998) and prepared in four steps namely sol-gel formation, solvent exchange, a supercritical drying and pyrolysis, all of these steps affect the structure of carbon aerogels (Jun Li et al., 2008).



**Figure 2.6** The reaction of Resorcinol with Formaldehyde.





**Figure 2.7** Effect of the pyrolysis on a of resorcinol-formaldehyde aerogel (a) before pyrolysis (b) after pyrolysis.

However, the conventional method is not suitable for commercial application because it involved a supercritical drying step which is very complicated, expensive and dangerous and use quite expensive raw material. Researchers have tried to produce carbon aerogels from cheap raw materials (phenol resorcinol-formaldehyde, phenolic-furfural, melamine-formaldehyde, polyurethanes, and polyureas) (Pekala *et al.*, 1998) and safety synthesis method (Li *et al.*, 2008).

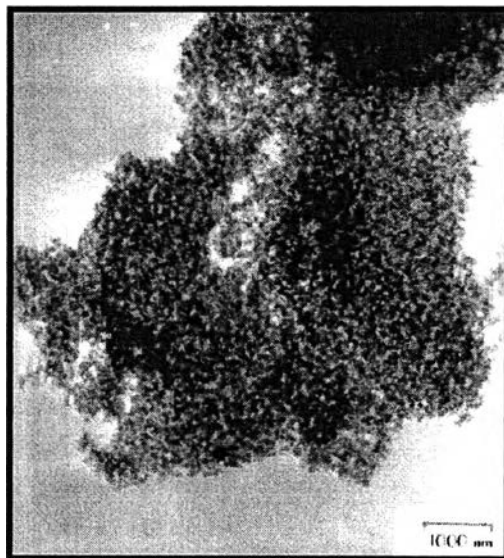
### 2.2.2 Structure and Properties of Carbon Aerogels

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 m<sup>2</sup>/g)
- Biocompatibility
- Anti corrosion by acid or base etc.

Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR), N<sub>2</sub> adsorption, Small-angle X-ray scattering (SAXS), Mechanical 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 from the viewpoint of their applications to adsorption, catalysis and electrochemical electrode (Tamon et al., 1999).



**Figure 2.8** Transmission Electronic Microscopic (TEM) of the carbon aerogel.

Resorcinol-formaldehyde (RF) aerogels were synthesized via the sol-gel polycondensation of resorcinol with formaldehyde in a slightly basic aqueous solution and followed by supercritical drying with carbon dioxide. Mesoporous carbon aerogels were then obtained by pyrolyzing the RF aerogels in an inert atmosphere. The control of mesoporous structure of the aerogels was studied by changing the amount of resorcinol (R), formaldehyde (F), distilled water (W) and sodium carbonate (basic catalyst) (C) used in the polycondensation. As a result of characterization by nitrogen adsorption, the mesopore radius of the RF aerogel was controlled in the range of 2.5–9.2 nm by changing the mole ratio of resorcinol to sodium carbonate (R/C) and the ratio of resorcinol to water used as diluent (R/W). Although the aerogels shrank by 1–4 nm during pyrolysis, the shape of pore size distribution of the RF aerogel was kept. It was found that the mesopore radius of carbon aerogel ranged from 2.0 to 6.1 nm. As the pyrolysis temperature increased, the peak radius of pore size distribution was kept the same despite the fact that the pore volume decreased because of shrinkage. Adsorption isotherms of ethane and

ethylene were measured on the aerogels prepared. As the pyrolysis temperature increased, the amounts of ethane adsorbed became larger than those of ethylene adsorbed on the aerogels. The aerogels pyrolyzed at 1000°C had the same adsorption characteristics of ethane and ethylene as the activated carbons did (Tamon *et al.*, 1998).

Horikawa *et al.* (2003) prepared discrete RF carbon aerogel particles with a spherical shape and controlled their diameter. They synthesized spherical resorcinol–formaldehyde (RF) aerogel particles were synthesized by emulsion polymerization of resorcinol with formaldehyde in a slightly basic aqueous solution, followed by supercritical drying with carbon dioxide. RF carbon aerogel particles were prepared by carbonizing of the RF aerogel particles at a high temperature under a nitrogen atmosphere. By changing the viscosity of the RF sol added to the cyclohexane containing a surface-active agent for preparation of the spherical RF hydrogels, they investigated the influence of the apparent viscosity of the RF sol on the size of the generated RF carbon aerogel particles. The RF carbon aerogel particles with a truly spherical shape and control their size in the range from about 10 to 500 nm were successfully prepared by changing the apparent viscosity of the RF sol. The spherical RF carbon aerogel particles with an average diameter of 20 nm have a BET surface area of about 800 m<sup>2</sup>/g and a uniform mesopore radius of 1.78 nm.

Shen *et al.* (2005) studied about the texture of resorcinol-formaldehyde (RF) and carbon aerogels derived from high RC ratio (molar ratio of resorcinol to catalyst) and supercritical drying. It was found that the RC ratio in the sol-gel process influenced the final structure of carbon aerogels which included the sizes of the particles and pores, specific surface areas and pore size distribution. The size of the particles and pores increases with the increase of RC ratio and with a high RC ratio typically 800 and above. The macroporous structure of RF aerogels could be controlled at ambient conditions. Compared with RF aerogels, carbon aerogels have larger specific surface areas, more micropores and different types of adsorption isotherms. Carbon aerogels dried at ambient conditions also have specific surface areas similar to that of carbon aerogels prepared by supercritical drying.

### 2.2.3 Application of Carbon Aerogel

#### 2.2.3.1 *Metal-doped Carbon Aerogel*

One area of significant interest in carbon aerogel research is the incorporation of metal species into the carbon framework with the goal of modifying the structure, conductivity and catalytic activity of the carbon aerogel. Three main strategies have been used to introduce metal species into the carbon framework. The first consists of dissolving the metal precursor in the initial resorcinol-formaldehyde mixture (Maldonado-Hodar *et al.*,1999). The second involves the use of a resorcinol derivative containing an ion exchange moiety that can be polymerized using sol-gel techniques. The repeating unit of the organic polymer contains a binding site for metal ions, ensuring a uniform dispersion of the dopant (Baumann *et al.*,2002). Finally, the third strategy is to deposit the metal precursor on the organic or the carbon aerogel. Different methods have been used for this purpose, such as incipient wetness, adsorption, sublimation and supercritical deposition.

Different metal-containing carbon aerogels have already been prepared and characterized, including Ce and Zr-doped carbon aerogels (Moreno-Castilla *et al.*,1999) and Cr-, Mo-,W-, Fe-, Ru-, Co-, Ni-, Pd-, Pt-, Cu- and Ag-containing carbon aerogels. The objective of these studies was to characterize these materials for their use as electrodes for electrical double-layer capacitors and as catalysts.

Ce-, Zr-doped carbon aerogels were obtained by dissolving their nitrates in an R/F mixture at different pHs (Bekyarova *et al.*,1999). The aerogels were carbonized at 1050°C. Introduction of the metal salts produced changes in the initial pH and, therefore, in the chemistry of the process. Some of the textural characteristics of these samples are compiled in Table 2.1. The surface area of these samples ranged from 87 to 800 m<sup>2</sup>g<sup>-1</sup>, the micropore volume from 0.03 to 0.20cm<sup>3</sup>g<sup>-1</sup> and the micropore size from 0.65 to 0.90 nm (Bekyarova *et al.*,2000). Synthesis of Zr-doped carbon aerogels resulted in microporous materials, whereas doping only with Ce yielded a material with very low microporosity. These results indicate that not only the initial pH of the solution but also the nature of the dopant

metal affected the sol-gel chemistry and, therefore, the structure of the solid. Transmission electron microscopy (TEM) observations showed that metals were distributed homogeneously throughout the material in the form of nanosized particles, despite the high temperature treatment of 1050°C. Authors suggested that dopant elements were anchored to the carbon structure, preventing their migration and growth.

**Table 2.1** Textural characteristics of Ce-, Zr-doped carbon aerogels (adapted from (Bekyarova *et al.*, 1999))

Sample	Weight loss (%)	$\alpha_s$ method		DR method	
		$S_{Total}$ ( $m^2 g^{-1}$ )	$S_{ext}$ ( $m^2 g^{-1}$ )	$W_0$ ( $cm^3 g^{-1}$ )	$L_0$ (nm)
d-CA	54	500	11	0.16	0.72
d-CA-1	14	1150	40	0.37	0.68
d-CA-3	45	1750	67	0.60	0.96
d-CA-5	82	2240	600	0.70	1.46

Pt-, Pd- and Ag-containing carbon aerogels were prepared by using an R/F molar ratio of 0.5, replacing the  $Na_2CO_3$  catalyst in the initial mixture with  $[Pt(NH_3)_4]Cl_2$ ,  $PdCl_2$  or  $AgOOCCH_3$  (Maldonado-Hodar *et al.*, 1999). The aerogels thus obtained were pyrolyzed at 1000°C in  $N_2$  flow and then steam activated at 900°C for 25 min. Some of the results obtained are shown in Table 2.2, showing the large meso- and macropore volumes of the steam activated Pt-containing aerogel. These textural characteristics were produced by the presence of a very small amount of Pt in the aerogel matrix. The large increase in mesoand macropore volumes,  $V_2$  and  $V_3$  respectively, of this sample was in part due to the high degree of activation, because Pt acted as gasification catalyst during the activation step. Thus, sample NC-S, with no metal in its composition, underwent a lower degree of activation and its meso- and macropore volumes were therefore less developed. In contrast, the steam activated Pd-containing carbon aerogel was essentially microporous ( $W_0$ ), and had the highest nitrogen surface area of the three samples.

**Table 2.2** Textural characteristics of steam activated metal-doped carbon aerogels and the blank (from (Maldonado-Hodar *et al.*, 1999))

Sample	Burn-off (%)	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	$W_0$ ( $\text{cm}^3\text{g}^{-1}$ )	$L_0$ (nm)	$V_2$ ( $\text{cm}^3\text{g}^{-1}$ )	$V_3$ ( $\text{cm}^3\text{g}^{-1}$ )
NC-S	25	1085	0.38	1.29	0.04	0.98
(N-Pt) C-S	60	699	0.35	1.26	0.82	2.98
(N-Ag) C-S	24	1140	0.41	1.37	0.00	0.46
(N-Pd) C-S	31	1302	0.42	1.36	0.00	0.03

In other Pt-doped monolithic carbon aerogels prepared by adding the Pt precursor to the initial R/F mixture (Maldonado-Hodar *et al.*, 2004), the Pt particle size determined by  $\text{H}_2$  chemisorption was much higher than that determined by high-resolution transmission electron microscopy (HRTEM). This indicates that some Pt particles were encapsulated by the carbon matrix and were consequently inaccessible to  $\text{H}_2$ .

Carbon aerogel is a novel carbon that possesses fully interconnected mesopores. Its density, pore volume and specific surface area can be controlled by synthetic process. The unique structure of carbon aerogel has attracted much interest in its application to catalysis. Hongda *et al.* (2007) a narrow pore size distribution centered at 11.4 nm, was used as catalyst support in Direct methanol fuel cells (DMFC) at first time. Different composition of Pt-Ru bimetallic catalyst could be loaded on carbon aerogel through a simple method. The metal particle size is around 3 nm, and disperses uniformly on the support. The high specific surface area of carbon aerogel facilitates the preparation process. With only two third of noble metal used, the membrane electrode assembly (MEAs) prepared by Pt-Ru/CA can reach the same power density of commercial catalyst in single DMFC test. This may be attributed to the mesopores of carbon aerogel promoting the mass transportation of methanol in catalyst layer. Temperature has great activation to Pt-Ru catalyst in which Ru has more effects at higher temperature. When the temperature is lower

than 40 °C, Pt–Ru bimetallic with less than 33 at.% Ru has better performance than that contains 50 at.% Ru.

#### 2.2.3.2 Catalytic Behaviour of Metal-doped Carbon Aerogels

To date, there have only been a few studies Cobalt-doped monolithic carbon aerogels were also used as catalysts in attempts to grow carbon nanotubes by CO decomposition at 860°C (Fu *et al.*,2003), since Co nanoparticles are often used as a catalyst for the growth of carbon nanofilaments and nanotubes. However, it was found that many round or variously curved carbon nanofilaments and graphitic nanoribbons grew on the surface of Co-doped carbon aerogels but that no nanotubes grew under these conditions. Furthermore, when the Co-doped carbon aerogel was carbonized at a temperature of 1050°C, the catalytic activity of the metallic Co particle produced the growth of a high density of graphitic nanoribbons with an 002 spacing of about 0.38 nm. This was previously reported by other authors (Maldonado-Hodar *et al.*,2000), not only with Co but also with Cr, Fe and Ni.

Pt catalysts supported on carbon aerogels were used in the toluene combustion reaction (Maldonado-Hodar *et al.*,2004). The carbon aerogels were obtained by carbonization of an organic aerogel at 500 and 1000°C. Both samples were mesoporous, and their microporosity was equally accessible to both N<sub>2</sub> and CO<sub>2</sub> at 196 °and 0°C, respectively. Pt was deposited on both carbon aerogels by an incipient wetness technique using an aqueous solution of [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>. The supported catalysts thus obtained were pretreated in different atmospheres to obtain different mean Pt particle sizes.

#### 2.2.4 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 250–600°C, which results from the release of water, organic groups an

simultaneous rearrangement of aromatic rings. A new band occurring at  $874\text{ cm}^{-1}$  in IR spectra after  $400^\circ\text{C}$  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).

### **2.3 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 ( $2 \text{ nm} \leq \text{pore size} \leq 50 \text{ nm}$ ) 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.