CHAPTER II

LITERATURE REVIEW

2.1 Membrane Technology

2.1.1 Inorganic Membranes

Inorganic membranes represent an alternative gas separation technology. However, it is not the purpose of this work to cover these membranes in detail. There are two major categories of inorganic membranes, porous and nonporous. Non-porous membranes are generally used in highly selective separation of hydrogen, where transportation is through alloys of palladium or oxygen through perovskite systems. Porous inorganic membranes are generally cheaper but less selective. The attractiveness of inorganic systems is their ability to operate at high temperatures. A particular high temperature operation of interest is the separation of carbon dioxide from hydrogen in syngas processes. The large size of carbon dioxide relative to hydrogen means that achieving a carbon dioxide rich permeate stream by simple molecular sieving is not possible. Inorganic membranes overcome this by functionalizing the pores of the membrane to increase the carbon dioxide loading. Permeability then becomes a function of surface diffusion (Scholes *et al.*, 2008).

2.1.2 Polymeric Membranes

Organic polymers are the most widely used materials in membrane gas separation. Recently, there have been more publications on systems that combine different polymers to produce membranes with improve CO_2/CH_4 permeances and selectivities. Polymeric membranes are generally nonporous. Gas permeation is occurred by the solution-diffusion mechanism which is determined by solubility and diffusivity of gases within the polymer matrix (Iarikov and Ted Oyama, 2011).

Li *et al.* (2013) developed the thin film composite membranes containing ethylene oxide groups by interfacial polymerization with trimesoyl chloride and commercial diamines named diethylene glycol bis(3-aminopropyl) ether (DGBAmE) and diaminopolyethylene glycol (DAmPEG). The structure and separation performance of membranes with short ethylene oxide units and long ethylene oxide units were compared, and the concentrations of monomers used in

interfacial polymerization were adjusted to optimize the structure and separation performance of membranes. The thin film composite membranes prepared with DGBAmE and DAmPEG were named EO-3 and EO-21 according to the length of ethylene oxide units, respectively. The results showed that the structure and separation performance of long ethylene oxide units are hardly optimized by simply increasing the concentration of DAmPEG, because in interfacial polymerization process, the long ethylene oxide units of DAmPEG not only decreased the diffusion rate of DAmPEG from aqueous phase to organic phase, but also hindered the diffusion of DAmPEG through the film for further reaction, which results in the extremely low crosslinked density of EO-21 and the deterioration of gas selectivity at high feed pressure. In contrast, the growth of interfacial polymerization formed layer of EO-3 was adequate due to the much shorter ethylene oxide units of DGBAmE. The structure and separation performance of EO-3 was conveniently adjusted by changing concentrations of monomers used in interfacial polymerization process. EO-3 prepared with optimized monomer concentrations displays attractive CO_2 permeance and CO_2 gas selectivity. It was evaluated that by using EO-3 in the two-stage membrane process, the high recovery and purity of the product can be achieved for the syngas and natural gas purification and the CO_2 capture from flue gas.

Polyimides are good candidates for using as gas separation membrane materials because they have a better permselectivity performance than membranes made from conventional glassy polymers such as cellulose acetate and polysulfone. However, one problem for CH_2/CH_4 separation using polymeric membrane is CO_2-induced plasticization. The polymer matrix swells upon sorption of CO_2, accelerating the permeation of CH_4. So the polymer membrane loses it selectivity (Horn, N.R. and Paul, D.R., 2011).

In 1998, Bos *et al.* succeeded in stabilizing the polymer membrane by a thermal treatment. They used polyimide Matrimid as a polymer membrane. The results showed that the crosslinking of Matrimid films by thermal treatment at 350 °C was a successful method to overcome CO_2-induced plasticization. Mixed gas permeation experiments revealed that the CH_4 permeability remained constant for the treated film. But the untreated film the CH_4 permeability strongly increased at higher CH_4 pressure due to the CO_2 plasticization.

Scholes *et al.* (2014) studied CO_2 separation from CH_4 by using thermal rearranged polybenzoxazole/polyimide blended membranes. The thermal rearranged process altered HAB–6FDA to form the corresponding thermal rearranged polybenzoxazole, while leaving 4MPD–6FDA unaffected. The results showed thermal rearranged blend membranes had improved mechanical strength compared to the thermal rearranged HAB–6FDA homopolymer, because of the presence of 4MPD–6FDA polyimide. The CO_2 solubility of the blend membranes varied little from that of the thermal rearranged HAB–6FDA homopolymer. The CO_2/CH_4 permselectivity of the blend membranes varied as a function of blend compositions, which was associated with changes in the fractional free volume affecting CO_2 diffusivity. It was observed that permselectivity increased with increasing 4MPD–6FDA content.

Li *et al.* (2010) studied silver ionic modification in dual-layer hollow fiber membranes to enhance CO_2/CH_4 separation. After the silver ion-exchange treatement, the results showed these silver ionic modified membranes possess higher resistance to the CO_2-induced plasticization than the as-spun counterparts. The possible reason was that both electrostatic crosslinking and steric hindrance cause an increase in packing density of polymer chains and a decrease in fractional free volume.

2.1.3 Composite Membranes

2.1.3.1 Supported Ionic Liquid Membranes

Supported Ionic Liquid Membranes (SILMs) are composed of ionic liquids impregnated into polymeric or inorganic supports. Room Temperature Ionic Liquids (RTILs) are special compounds that can be characterized as organic salts that are liquid at room temperature (Iarikov and Ted Oyama, 2011). The advantage of ionic liquids are high thermal and chemical stability, non-frammability, miscibility with water and organic solvents and negligible vapor pressure (Malik *et al.*, 2011).

Uchytil *et al.* (2011) studied the transport of carbon dioxide and methane in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf$_2$N]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf$_2$N]) ionic liquid membranes with different ionic liquid amounts. They

found that the gas permeability increased with the ionic liquid [emim][Tf$_2$N] content in the membrane. But the gas permeability in both ionic liquids was quite low especially methane permeability. It meant that the gas flux through the supported liquid membranes was strongly limited.

In 2014, Shahkaramipour *et al.* studied the influences of temperature and pressure on the permeability and selectivity of CO$_2$/CH$_4$ by using alumina-supported ionic liquid membranes. Two ionic liquids, pr[mim]$_2$[Tf$_2$N]$_2$ [1,3-di(3-methyl-imidazolium) propane bis(trifluoromethylsulfonyl) imide and h[mim]$_2$[Tf$_2$N]$_2$[(1,6-di(3-methylimidazolium) hexane bis (trifluoromethylsulfonyl) imide), were synthesized and stabilized on an alumina porous support. The results showed that partial pressure of diffusing gas through supported ionic liquid did not have any effect on permeability of two gases for two ionic liquids. But permeability of gases increased with increasing temperature. Because these two ionic liquids had high viscosity, so the permeability was affected when temperature increased. In this work, the viscosity of ionic liquids played a major role in permeation mechanism.

However, the negative aspect of supported ionic liquid membranes is the leaching of the ionic liquid from the support because of the pressure gradient across the membrane.

2.1.3.2 Mixed-matrix Membranes

Mixed-matrix membranes consist of inorganic particles incorporated into a continuous polymer matrix. Gases are transported through both polymeric and inorganic phases. Inorganic particles can act as molecular sieves, disrupting the polymer structure thus increasing the permeance, or serve as a barrier, reducing gas permeance (Iarikov *et al.*, 2011).

Li *et al.* (2007) introduced silver ion-exchange treatment of zeolite to change the physical and chemical adsorption properties of penetrants in the zeolite. Polyethersulfone (PES)-zeolite NaA mixed matrix membranes (MMMs) and PES–zeolite AgA MMMs were fabricated at high processing temperatures with different zeolite loadings. The effects of silver ion-exchange treatment of zeolite and zeolite loadings on the gas separation performance of these MMMs were investigated. CO$_2$ permeability of PES–zeolite AgA MMMs was higher than that of PES–zeolite NaA MMMs, whereas their CH$_4$ permeability was lower than that of

PES–zeolite NaA MMMs. This trend was the result of the reversible reaction between silver ion and CO_2 molecule. CO_2 and CH_4 permeability of PES–zeolite AgA MMMs decreased with increasing zeolite content arising from the effects of partial pore blockage of zeolite and polymer chain rigidification, whereas their CO_2/CH_4 selectivity increased with an increase in zeolite loadings and the highest value reached 59.6 at 50 wt% zeolite loading because of a combined effect of the facilitated transport mechanism of silver ion and the molecular sieving mechanism of zeolite.

2.2 Membrane Gas Separation Performance

Membrane separation performance is evaluated based on gas permeance and selectivity. Membrane permeance is expressed as the amount of gas that goes through a membrane of known area per unit time per cross-membrane pressure. Selectivity is defined as the ratio of single-gas permeances of any two species permeating through the membrane and is used as a measure of separation efficiency (Iarikov et al., 2011).

Gas permeation through a dense membrane takes place according to the well-known solution-diffusion mechanism (Wijmans et al., 1995)

$$P_i = S_i \times D_i \tag{2.1}$$

where the permeability coefficient P_i in Barrer (1 Barrer = 10^{-10} cm^3 (STP)cm/(cm^2 s cmHg) = 3.34×10^{-16} mol m/(m^2 s Pa)) is the product of the solubility coefficient (S_i) (cm^3(STP)/(cm^3 bar)) and the diffusion coefficient (D_i) (cm^2/s) of component i.

The selectivity of a gas pair is the ratio of their permeability coefficients:

$$\alpha_{ij} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{2.2}$$

where D_i/D_j is the diffusion selectivity and S_i/S_j the solubility selectivity of components i and j, respectively. Diffusion coefficients increase with decreasing penetrant size, increasing polymeric fractional free volume, increasing polymer chain flexibility, increasing temperature and decreasing polymer penetrant interactions. On

the other hand, solubility coefficients increase with increasing polymer penetrant interactions, decreasing temperature and increasing condensability of the penetrant (Ploegmakers *et al.*, 2013).

2.3 Polybenzoxazine

Polybenzoxazines are a new type of thermosetting phenolic resins. They have better properties over conventional novolac and resole type of phenolic resins because they have thermal and frame retardant properties of phenolics along with good mechanical properties and molecular design flexibility. Moreover, the unique properties of polybenzoxazine are near-zero shrinkage, reasonably high char yield, fast development of mechanical properties as a function of conversion, glass transitions much higher than curing temperatures, excellent electrical properties, and low water absorption despite having many hydrophilic groups.
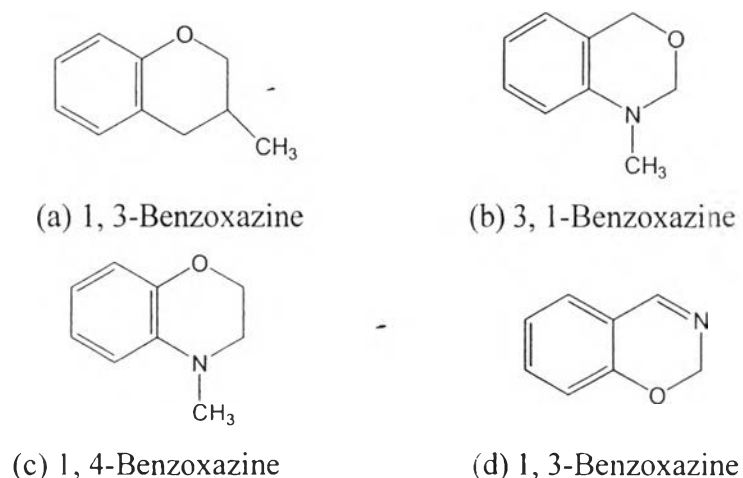

(a) 1, 3-Benzoxazine   (b) 3, 1-Benzoxazine

(c) 1, 4-Benzoxazine   (d) 1, 3-Benzoxazine

Figure 2.1 Various structures of benzoxazine molecules. (a) 3-methyl-2H, 4H-benzo[e]1,3-oxazine; (b) 1-methyl-2H,4H-benzo[d]1,3-oxazine; (c) 4-methyl-2H,3H-benzo[e]1,4-oxazine; and (d) 2H-benzo[e]1,3-oxazine.

Benzoxazine is a molecule where an oxazine ring (a heterocyclic six-membered ring with oxygen and nitrogen atom) is attached to a benzene ring. There are several benzoxazine structures depending on the position of the heteroatoms as shown in figure 2.1 (Ishida, 2011)

2.3.1 Chemical Methodologies for Synthesis of Benzoxazine Monomer

Benzoxazine monomers are typically synthesized by the reaction of phenol, amine and formaldehyde. However, various types of benzoxazine monomer can be synthesized by using various phenols and amines with different substitution groups attached.

Holly *et al.* (1944) first reported the synthesis of monofunctional benzoxazine monomers through the condensation reaction of primary amines with formaldehyde and substituted phenols. Thus, monofunctional benzoxazine monomers as precursors for polybenzoxazine offer limited usefulness as structural materials; however, they might be useful as reactive diluent to facilitate the processing. (Figure 2.2)
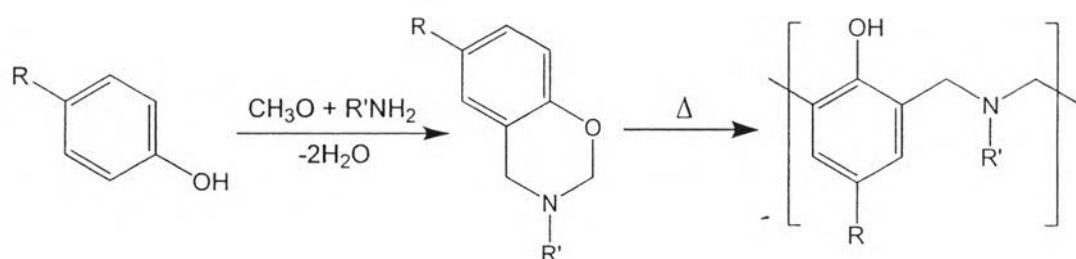

Figure 2.2 Synthesis of monofunctional benzoxazine.

Liu *et al.* (2011) studied the thermally accelerated ring-opening polymerization of bifunctional benzoxazine monomers and the properties of their cross-linked polymers. Bifunctional benzoxazines offer greater flexibility in molecular design than monofunctional monomers and hence a wide variation in the performance of polybenzoxazines can be achieved. This family of bifunctional benzoxazine monomers is classified into two classes; the first class is bisphenol-based bifunctional benzoxazine monomer which is produced by the reaction of bisphenol with either aliphatic or aromatic monofunctional primary amine as shown in figure 2.3. Another class of bifunctional benzoxazines is diamine based bifunctional benzoxazine monomers, which can be synthesized by the reaction of aromatic or aliphatic diamines with a monofunctional phenolic structure of ortho-vacant position as shown in figure 2.4.
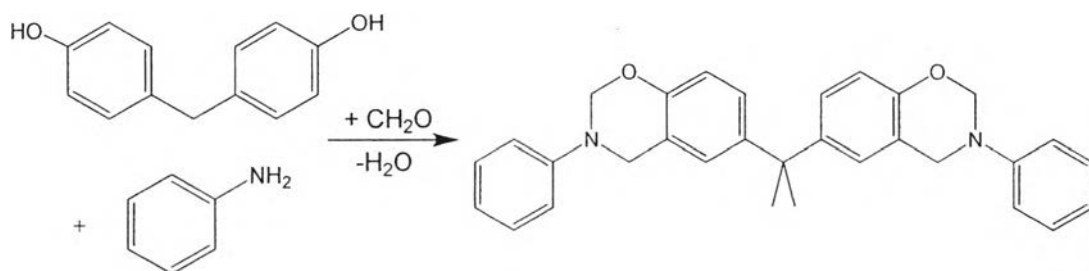
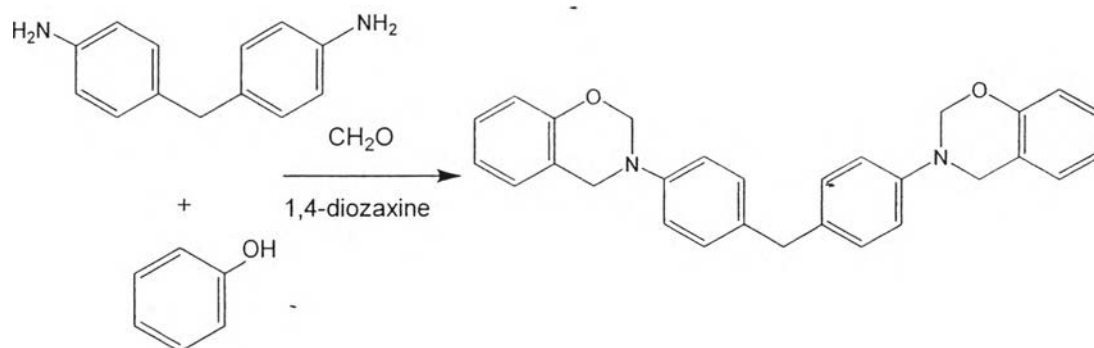**Figure 2.3** Synthesis of bisphenol A- and methylamine-based benzoxazine.

Figure 2.4 Synthesis of methylenedianiline (DDM)-based benzoxazine monomer (P-ddm).

The use of aromatic diamines for the synthesis of bifunctional benzoxazine monomer may have problem because of the poor solubility of most aromatic diamines in the common preferred solvents used for benzoxazine synthesis and the formation of insoluble side products resulting from perhydrotriazene structures as - intermediate of the condensation of aromatic diamines and formaldehyde. Agag *et al.* (2011) reported a new approach to minimize this perhydrotriazene intermediate problem by using nonpolar high boiling point solvent for monomer synthesis. They prepared 4,4-diaminodiphenyl sulfone-based bifunctional benzoxazineas, an example of difficult benzoxazine monomers, in xylenes as nonpolar high boiling solvent. Multifunctional amines or phenolic derivatives can also be used to synthesize multifunctional benzoxazines.

2.3.2 Preparation of High Molecular Weight Benzoxazine Precursors

Polymerization of benzoxazines through the ring-opening of the cyclic monomers only by heat treatment without the need of catalyst and without generating byproducts or volatiles, and thus excellent dimensional stability is obtained. The structure of a typical benzoxazine monomer (B-a) prepared from bisphenol-A, aniline and formaldehyde along with the structure of its polybenzoxazine (PB-a) are shown in figure 2.5.
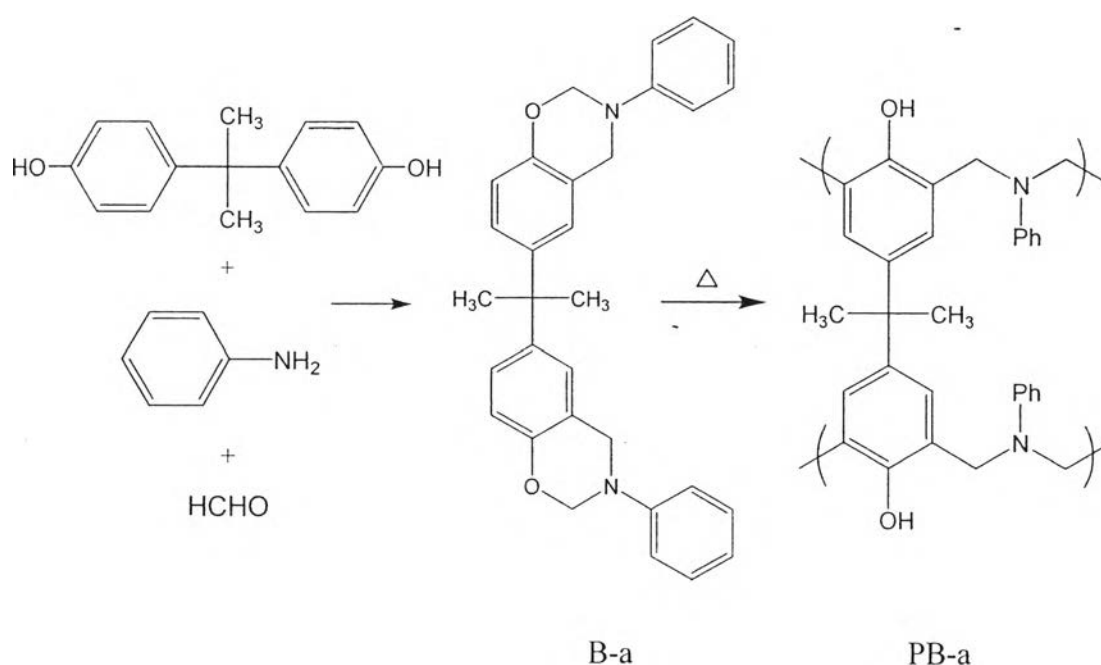

B-a   PB-a

Figure 2.5 Structures of B-a and PB-a.

High molecular weight polybenzoxazine precursors have been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde in figure 2.6. The precursor solution was cast on a glass plate, giving transparent and self-standing precursor films, which were 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 improved when compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films showed that polybenzoxazine from aromatic diamine presented the highest strength and modulus, while

polybenzoxazine from longer aliphatic diamine had higher elongation at break. The glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were as high as 238–260 °C. Additionally, these novel polybenzoxazine thermosets exhibited excellent thermal stability (Takeichi *et al.*, 2005).
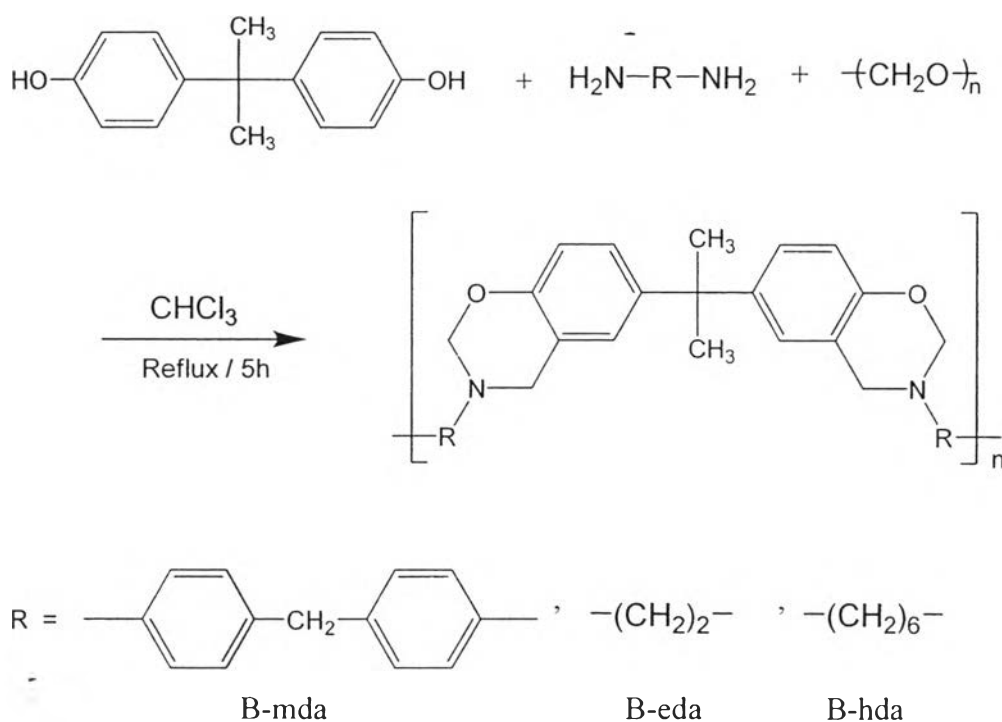

Figure 2.6 Preparation of polybenzoxazine precursors.

2.3.3 Applications of Polybenzoxazines

Polybenzoxazines can be used in many applications because of theirs high performance properties. Polybenzoxazines provide characteristics found in the traditional phenolic resin such as high heat resistance and frame retardance. In addition, they also provide characteristics that are not found in the traditional phenolics resins such as excellent dimensional stability, low water absorption and good dielectric properties (Takeichi T. *et al.*, 2008).

Lorjai *et al.* (2009) prepared polybenzoxazine foam and its transformation to carbon foam with a noncomplex and economical foaming method by using azodicarboamide (AZD) as a foaming agent. The results showed that

polybenzoxazine foams and carbon foams had uniform microstructure. Polybenzoxazine foams showed a density in the range of 273-407 kg/m^3, and a compressive strength and a compressive modulus in the range of 5.2-12.4 MPa and 268-681 MPa, respectively. After carbonization of the benzoxazine foam at 800 °C, the carbon foam with superior compressive properties was obtained.

Pakkethati *et al.* (2010) developed polybenzoxazine membrames for ethanol-water separation via pervaporation system. Polybenzoxazine membranes were synthesized from bisphenol-A, formaldehyde and three different types of diamine: hexamethylenediamine (hda), tetraethylenepentamine (tepa) and tetraethylenetriamine (teta) via a quasi-solventless method. The experimental results showed that the membrane derived from poly(BA-hda) showed the longest service time when compared with those prepared from poly(BA-tepa) and poly(BA-teta). The best temperature of the feed solution and the thickness of the poly(hda) membrane for ethanol/water separation were 70 °C and 200 µm, respectively. The total permeation flux of water through the 200 µm thick poly(BA-hda) was 1.52 kg/m^{2}h and its separation factor for the ethanol-water system was found to be higher than 10,000.

Katanyoota *et al.* (2010) used polybenzoxazine to prepare carbon aerogels used as an electrode for supercapacitors. Two types of polybenzoxazines derived from two different amines; aniline and triethylenetetramine denoted as BA-a and BA-teta, respectively, were chosen as the reactants for the organic precursor preparation. It found that the surface area of carbon aerogels from both BA-a and BA-teta was 391 and 368 m^2/g, respectively. The pore size of each carbon aerogel was in the range of 2–5 nm, which is a suitable pore size for use as electrodes in electrochemical applications. The electrochemical properties of the obtained carbon aerogels showed good performance for supercapacitor applications with a specific capacitance of 55.78 and 20.53 F/g for BA-teta and BA-a, respectively. At low voltage scanning, 1 and 5 mV/s, the cyclic voltammogram of the carbon aerogel derived from BA-teta gave a better rectangular shape than that of the other carbon aerogel due to a larger amount of mesopores.