



CHAPTER II

LITERATURE REVIEW

2.1 Polybenzoxazine

A series of polybenzoxazines obtained by the ring-opening polymerization of cyclic monomers, benzoxazines, have been developed as a novel type of phenolics resins. The monomers can be easily prepared from mono/diphenols, formaldehyde and various amines such as aniline, allylamine, and aminophenyl propargyl ether, etc. A wide variations of raw materials; phenols and amines, allow considerable molecular-design flexibility for the cyclic monomers. Polymerization proceeds through the ring-opening of the cyclic monomers only by heat treatment without the need of catalyst. Moreover, no byproducts or volatiles generated, and thus excellent dimensional stability is obtained. Polybenzoxazines provide characteristics found in the traditional phenolic resins such as high heat resistance and flame retardance. Interestingly, 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. Therefore, polybenzoxazines are a great candidate for various applications including materials used in electronic packaging or as a matrix of polymer composites. Nevertheless, there are still some shortcomings. The cured materials are brittle. Additionally, a relatively high temperature is required for the ring-opening polymerization. Also, due to their brittleness, polybenzoxazine derived from monomers can not be easily processed into thin films (Takeishi *et al.*, 2005).

Aiming for performance enhancement and lowering the polymerization temperature, various approaches have been investigated. One approach is the modification of monomer. Introduction of another crosslinkable functional units is very effective to enhance the thermal properties (Kim *et al.*, 1999). As another approach, polymer alloys of polybenzoxazine with high performance polymers or with elastomers resulted in high performance and tough films (Ishida *et al.*, 1996). Hybridization with inorganic materials such as layered clay (Agag *et al.*, 2000) and metal oxide nanoparticles (Agag *et al.*, 2004) was also successful in obtaining polybenzoxazine with improved properties. The toughness of the crosslinked

polybenzoxazine films from the high molecular weight monomer was greatly enhanced compared with the cured film from the typical low molecular weight monomer (Takeichi *et al.*, 2005).

2.1.1 Chemical Methodologies for Synthesis of Benzoxazine Monomer

Holly *et al.* (1944) first reported the synthesis of benzoxazine monomers via the condensation reaction of primary amines with formaldehyde and substituted phenols. The reaction was performed in a solvent in a two-step method using solvent. Later, Burke *et al.* (1949) found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound yielding a Mannich-bridge phenolic structure. In 1965, the same research group (Burke *et al.*, 1965) synthesized Mannich condensation of benzoxazine synthesis via a solvent approach. At first amine was added to formaldehyde at low temperature (10°C) to form an N,N-dihydroxymethylamine derivative product which then further reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring as shown in Figure 2.1.

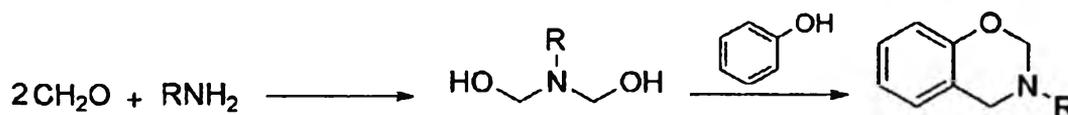


Figure 2.1 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

However, the curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with an average molecular weight around 1000 Da. Thus, materials with good performance could not 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, Ishida and coworkers have developed a new class of difunctional or multifunctional benzoxazine monomers. The precursor was synthesized using bisphenol-A, formaldehyde and

aniline, 1,4-dioxane was used as a solvent and the pure monomer was referred as B-a and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a were analyzed by ¹H-NMR measurements. The overall synthetic procedure is shown in Figure 2.2 (Ning and Ishida, 1994). 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. To achieve successful processing, the cure kinetics of this material was investigated by using DSC. The results indicated that the curing of benzoxazine precursors is an autocatalyzed reaction until vitrification is occurred (Ishida *et al.*, 1995).

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 the solvent synthesis approach. 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 (U.S. Patent, 1996) developed a solventless synthesis in the melt state.

The reaction mechanism and kinetics of this solventless synthesis were proposed by Liu *et al.*, (1995). In a typical 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 causing the 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 improvement of reaction times

compared with the traditional synthetic route and formation of fewer intermediates and by-products as contaminants.

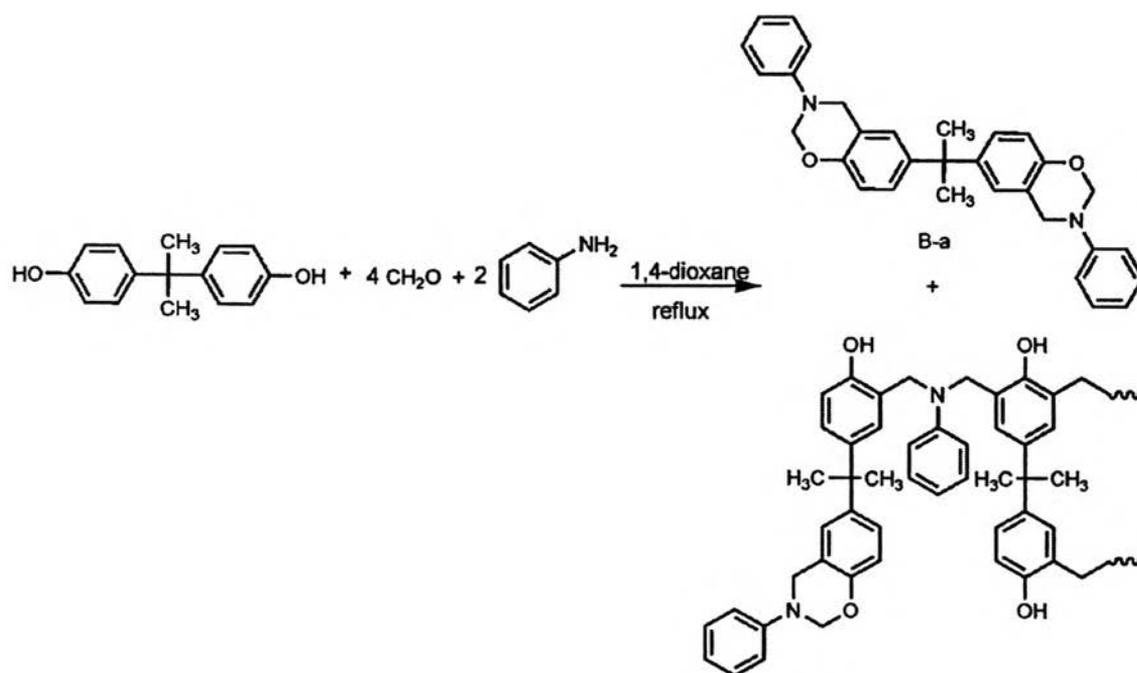


Figure 2.2 Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.

Various types of benzoxazine monomers can typically be synthesized using derivative phenols and amines (aliphatic or aromatic) with different substitution as starting materials in the presence of formaldehydes, by employing solution or solventless methods.

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 polybenzoxazine precursors have been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde in Figure 2.3. The precursors were obtained as soluble white powder. The structure of the precursors was confirmed by IR, ^1H 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 $240\text{ }^\circ\text{C}$ 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 precursors were as high as $238\text{--}260\text{ }^\circ\text{C}$. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability (Takeichi *et al.*, 2005).

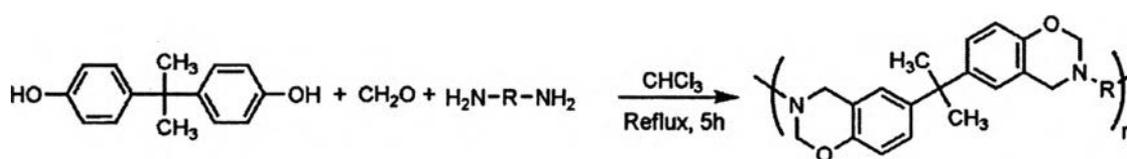


Figure 2.3 Synthesis of polybenzoxazine precursors.

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. They have obtained self-standing thin films from the precursors 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.

2.1.3 Improvement of The Crosslinking Densities

Despite the aforementioned advantages of polybenzoxazines obtained through benzoxazine monomer, the crosslinking densities of their networks are considered to be rather low because of intensive hydrogen bonding restricting segmental mobility and hence hindering network extension (Reiss *et al.*, 1997; Ishida *et al.*, 2001). Further increasing the crosslink density of the polybenzoxazine network is expected to enhance both the thermal and mechanical performance. A common approach can be achieved by copolymerization through the addition of another reactive comonomer through the phenolic group, such as epoxy resin (Ishida *et al.*, 2005), bisoxazoline (Kimura *et al.*, 1999), or hydroxyphenylmaleimide (Agag *et al.*, 2001). However, these binary systems require higher cure temperatures than neat polybenzoxazine, and the obtained viscosities sometimes increase because of the high melting point of some additives, which hinders the processing. Another approach for increasing the crosslinking density is introducing another polymerizable group into the benzoxazine structure. Several benzoxazine monomers containing specific functionalities such as ethynyl or phenyl ethynyl (Kim *et al.*, 1999), nitrile (Brunovska and Ishida, 1999), propargyl (Agag and Takeichi, 2001), and allyl groups (Agag *et al.*, 2005) have been reported. These monomers yielding high-performance polybenzoxazines with much higher glass transition temperatures (T_g) and improved decomposition temperatures in comparison with typical polybenzoxazines.

2.2 Bioethanol (Gasohol)

Biomass is one of the renewable energy resources, which exists in different forms. One of these clean forms of renewable energy is biofuel that includes biodiesel, bioethanol, biomethanol, biogas, etc. These fuels are produced from agricultural and industrial waste with a very low prime cost. At present many technical problems of combined heat and power with internal combustion engine (ICECHP) using biofuel have been solved (Ameri *et al.*, 2007). In the developed countries, ICECHP is a well established method (Fisher, 2003).

Bioethanol can be used in a multi-zone spark ignition (SI) engine as pure or by blending with gasoline (Al-Hasan, 2003; Bayraktar, 2005; Song *et al.*, 2006; Yucesu *et al.*, 2007; Yucesu *et al.*, 2006; Hsieh *et al.*, 2002). Moreover, a blending of bioethanol and gasoline (gasohol) at low concentration, does not require any change can design. Moreover, using gasohol in the engine can improve the engine performance and exhaust emissions (Yucesu *et al.*, 2006; Hsieh *et al.*, 2002; Pouloupoulos *et al.*, 2001; Pouloupoulos *et al.*, 2003; Al-Farayedhi *et al.*, 2004).

Gasohol which is a mixture of gasoline and ethanol, has higher octane number or better antiknock properties than gasoline. Additionally, it burns more slowly and completely, resulting in reduced emissions of some pollutants. However, ethanol-based gasohol with higher concentration of ethanol can damage rubber seals and diaphragms (Thiago *et al.*, 2007).

2.2.1 Types of Bioethanol

2.2.1.1 E10

E10 is a fuel mixture of 10% ethanol and 90% gasoline that can be used in the internal combustion engines of most modern automobiles and light-duty vehicles without need for any modification on the engine or fuel system. E10 blends are typically rated as 2 to 3 octane number higher than regular gasoline and are compatible with all new US automobiles.

2.2.1.2 E15

E15 contains 15% ethanol and 85% gasoline. This is generally the highest ratio of ethanol to gasoline that is possible to be used in vehicles

recommended by auto manufacturers to run on E10 in the US, though it is possible that many vehicles can handle higher mixtures without any problem.

2.2.1.3 E20 and E25

E20 contains 20% ethanol and 80% gasoline, while E25 contains 25% of ethanol. These blends have been widely used in Brazil since the late 1970s. As a response to the 1973 oil crisis, the Brazilian government regulated the use of the blend of ethanol fuel with gasoline as the engine fuel. The blend ratio was fluctuated between 10-22% of ethanol from 1976 upto 1992. Due to this mandatory, the pure gasoline is no longer available in Brazil since 2003, these limits were fixed at a maximum of 25% (E25) and a minimum of 20% (E20) of ethanol by volume are required. Later, the Brazilian government has set the percentage of the ethanol blend ratio according to the results of the sugarcane harvest and ethanol production from sugarcane, resulting in blend variations even within the same year. From July 2007, the mandatory blend was set at 25% of anhydrous ethanol (E25) which, has been the standard gasoline blend sold throughout Brazil.

2.2.1.4 E70 and E75

E70 contains 70% ethanol and 30% gasoline, while E75 contains 75% of ethanol. These are the winter blends used in the United States and Sweden for E85 flexible-fuel vehicles during the cold weather, but still sold at the pump labeled as E85. The seasonal reduction of the ethanol content to a E85 winter blend is mandated to avoid cold starting problems at low temperatures.

2.2.1.5 E85

E85 is a mixture of 85% ethanol and 15% gasoline, and is generally the highest ethanol fuel mixture found in the United States and several European countries, particularly in Sweden, as this blend is the standard fuel for flexible-fuel vehicles. This mixture has an octane rating of about 105, which is significantly lower than pure ethanol but still much higher than normal gasoline 87 octane.

2.2.1.6 E95

E95 designates a blend of 95% ethanol and 5% ignition improver and is used in some diesel engines where high compression is used to ignite the fuel, as opposed to the operation of gasoline engines where spark plugs are used.

Because of the high ignition temperatures of pure ethanol, the addition of ignition improver is necessary for successful diesel engine operation.

2.2.1.7 E100

E100 is pure ethanol fuel. Hydrated ethanol as an automotive fuel has been widely used in Brazil since the late 1970s. The ethanol used in Brazil is the azeotrope (the highest concentration of ethanol that can be achieved via distillation) and contains 4% of water.

2.3 Pervaporation Separation of Ethanol/Water

Partial vaporization of a liquid through a dense polymeric membrane is called pervaporation (Favre, 2003). Compared with distillation, pervaporation can often be considered a better candidate for separation of close boiling, azeotropic or isomeric mixtures (Verkerk *et al.*, 2001). For removal of volatile organic compounds, other separation technologies such as distillation, liquid–liquid extraction, carbon adsorption and air stripping are not applicable because of feed condition limitations, large volume of byproducts or high cost of post-treatments. However, pervaporation is not limited by these factors (Kim *et al.*, 2002). Currently, industrial applications of pervaporation are grouped into two categories : one is dehydration of alcohols and other organic solvents using hydrophilic or charged polymeric membranes and the other is the removal of small quantities of volatile organic compounds from water using hydrophobic membranes (Zhang *et al.*, 1992).

For polymeric pervaporation membranes, extensive researches were performed to find an optimized membrane material having selective interaction with a specific component of feed mixture to maximize separation performance in terms of separation factor, flux and stability. Polymer membranes can exhibit the selectivity based on the solubility and diffusion constant (Atra *et al.*, 1999). Thus, the choice of the membrane is very important since the efficiency of pervaporation depends greatly on the membrane used. Any formation of a liquid permeate film in the pores would inhibit the driving force (Sander *et al.*, 1986). For example, the hydroxy group is considered to interact strongly with water through hydrogen bonding membrane containing such a hydroxy group may be able to permeate water

with high separation factor (Chiang and Hu, 1991). A trade-off normally exists between the flux and the separation factor. Consequently, membranes are frequently developed to yield good fluxes and high separation factors simultaneously (Wijmans, 2003).

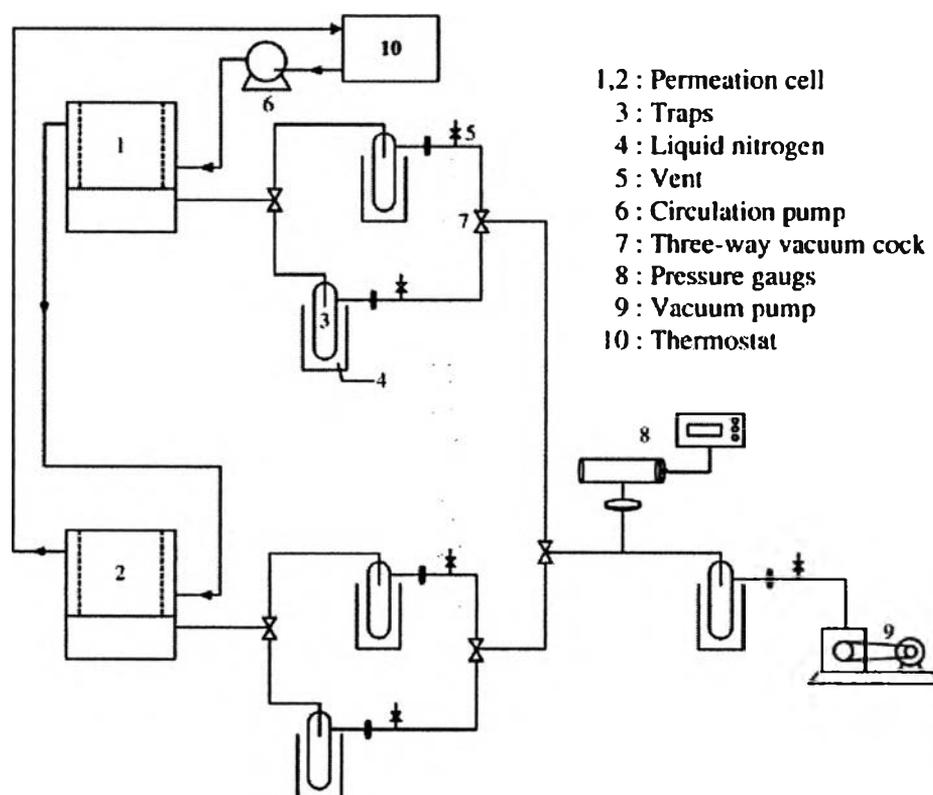


Figure 2.4 Schematic diagram of the pervaporation set-up.

However, the performance of these membranes is strongly influenced by process conditions such as feed concentration and temperature (Verkerk *et al.*, 2001). Silicone containing polymers were generally found to exhibit good organophilicity. Silicone rubber (mainly polydimethylsiloxane) based membranes were investigated for separation of organic aqueous mixtures such as alcohols, ketons, phenols and chlorohydrocarbones (Zhang *et al.*, 1992; Jiratananon *et al.*, 2002; Watson and Payne, 1990). Permeation of molecules through a dense non-porous polymer matrix is generally governed by the sorption–diffusion mechanism. Relative sorption of

permeants in membrane depends on their relative solubility in the membrane. Extents of solubility or miscibility of a component in or with polymeric membranes can be explained by the solubility parameter theory. Solubility parameter was defined by Hildebrand and Scott using “cohesive energy density” which is a measure of cohesive force that holds molecules together in liquid phase (Mandal and Pangarkar, 2002).

Water/alcohol separation is a well-known example of pervaporation process in chemical industry (Xu *et al.*, 2003). Separation of alcohol/water mixtures by pervaporation is important for obtaining liquid used as fuel from biomass sources. Many authors reported pervaporation process principals and experimental results using different types of hydrophobic membranes. Huang *et al.*, (2001) used a sulfonated poly (ether ether keton) membrane and Molina *et al.*, (2002) used CMG-OM-010 and 1060-SULZER membranes (alcohol concentration was varied between 13 and 20 wt% in water). In this research, an attempt was made to report effect of concentration and temperature on pervaporation of methanol and ethanol mixtures (alcohol concentration was varied between 0.3 and 3 wt% in water) on the separation efficiency using a hydrophobic flat-plate composite membrane with a dense skin layer of polydimethylsiloxane. The results showed both mixtures, increasing alcohol concentration increases permeation fluxes of both alcohols and water, however, water flux increases more significantly than alcohol fluxes resulting in a separation factor reduction. This can be due to the fact that increasing alcohol concentration increases membrane-free volume and simultaneously side chain mobility increases. Effect of temperature on PV of methanol/water and ethanol/water mixtures through PDMS membrane showed that total permeation flux of ethanol/water mixture was slightly higher than that of methanol/water mixture and the separation factor of ethanol was less than that of methanol because of their different molecular sizes and also solubility parameters (Kuo).