

CHAPTER II

LITERATURE REVIEW

2.1 Polybenzoxazine

Polybenzoxazine is a novel type of phenolic resins obtained by the thermally activated ring-opening polymerization of cyclic benzoxazines monomers which can be typically synthesized by using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials via either solution or solventless method. The structure of polybenzoxazines offers great design flexibility which allow the properties of the cured materials to be tailored for a wide range of applications (Ghosh N.N *et al.*, 2007) including electronic part, high performance composites, construction materials, and parts of airplane, etc. These properties can be obtained by varying either phenol or amine derivatives. Moreover, polybenzoxazines production also have many advantages such as polymerization can be completed through the ring-opening of the cyclic monomers only by heat treatment without the strong acid catalysts, no release of by-products, near-zero volumetric change upon curing, high char yield, and for some polybenzoxazines T_g much higher than cure temperature.

However, polybenzoxazine usually suffers from brittleness and can not be easily processed into thin films (Takeichi *et al.*, 2005). Various approaches have been used to overcome this problem and to further improve the properties of polybenzoxazine including modification of monomer with various types of phenol and/or amine. The followings are the summarized studies on the improvement of polybenzoxazines.

2.1.1 Chemical Methodologies for Synthesis of Benzoxazine Monomer

Holly *et al.* (1944) firstly reported the synthesis of mono-functional benzoxazine via the condensation reaction of primary amines with formaldehyde and substituted phenols. According to the reported procedure, this reaction was performed in solvent in two-steps. Later, they found that the benzoxazine ring

reacted preferentially with the free ortho positions of a phenolic compound yielding a Mannich-bridge phenolic structure (Burke *et al.*, 1949) which is shown in Figure 2.1

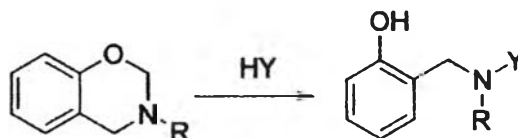


Figure 2.1 Ring opening of benzoxazine in acidic medium.

The mechanism of synthesis starts by first addition of amine to formaldehyde at low temperature to form an N,N-dihydroxymethylamine derivatives and further reacts with the labile hydrogen of the hydroxyl group which is in the ortho position of the phenol at the elevated temperature to form the oxazine ring as shown Figure 2.2

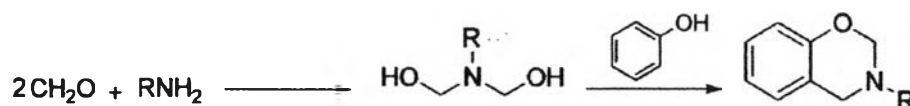


Figure 2.2 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

It can be observed that the presence of a compound with active hydrogen (HY) is necessary for the ring opening of some benzoxazines, such as naphthol, indoles, carbazole, imides, and aliphatic nitro compounds, even phenol which is one of the starting compounds for synthesis (Burke *et al.*, 1952).

Moreover, Ishida *et al.* (1996) and Macko *et al.* (2001) also studied the synthesis of polybenzoxazine by using phenol derivatives as starting materials such as phenol, 1,3,5-trihydroxybenzene, polyvinylphenol, 2-allylphenol, dimethylphenol, and 4-hydroxybenzophenone, *p*-cresol. 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 and for many applications 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 and Burke *et al.*, 1952). Like the report of Takeichi *et al.* (2005) that the mono-functional benzoxazines monomers usually suffers from brittleness that can not be easily processed into thin films.

Ishida and coworkers have developed a new class of difunctional or multifunctional benzoxazine monomers with the ring opening reactions in different solvents being initiated by dimers and higher oligomers in the resin composition (Ishida *et al.*, 1996). The resulting product was a monomer with difunctional benzoxazine ring structure at both ends of 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. They also found that the composition of the products is, to a large extent, dependent on the polarity of the solvent. Therefore, solvent method was 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). However, the slow reaction rate or large amount of solvent required for the synthesis and, in some case, the poor solubility of the precursors are the major disadvantages of solution method. Moreover, this method also increase cost of products and environmental problems due to using organic solvent, and have problems during processing from the solvent residue in the precursors. Later, Ishida *et al.* (1996) developed the solventless synthesis to overcome these shortcoming by mixing the reactants i.e., aldehyde, amine and phenolic precursors. The reaction mechanism and kinetics of this solventless synthesis were proposed by Liu *et al.*, (1995). In a typical synthesis, the reactants can physically mixed together with heating to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine.

2.1.2. Polybenzoxazines

The synthesis by changing phenol to bis-phenol-A and using aromatic or aliphatic diamine by solution synthesis are the important way to increase the benzoxazine molecular weight. Takeichi *et al.*, (2005) prepared polybenzoxazines by varying three types of diamine, ethylenediamine (eda), hexamethylenedianiline (hda) and methylenediamine (mda) compared with typical diamine, and formaline. Transparent thin precursor films were easily obtained by casting the precursor solution on a glass plate which shown in Figure 2.3.

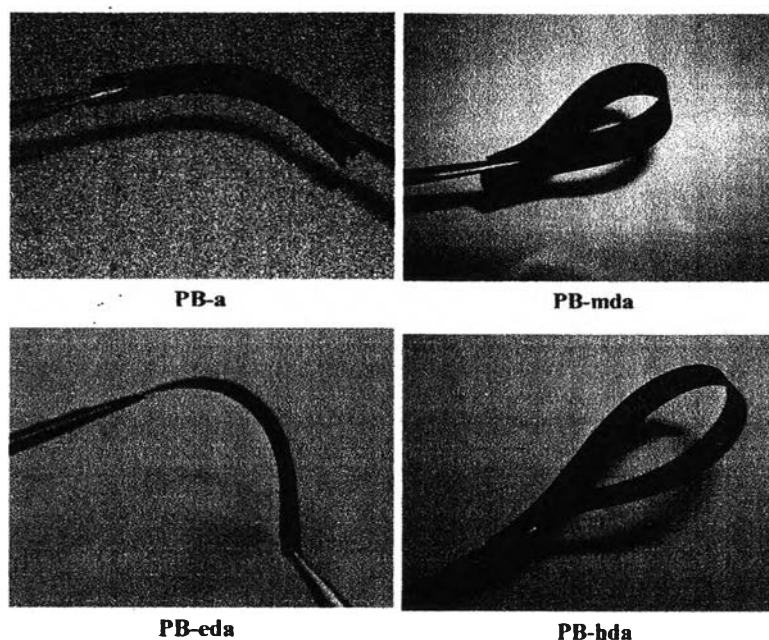


Figure 2.3 Appearance of polybenzoxazine films.

The polybenzoxazine films from the high molecular weight precursors exhibited significantly improved toughness than the typical polybenzoxazine due to the long linear backbone and high crosslinked density. Moreover, the T_g values of these polybenzoxazine were 238-260 °C which were higher than the T_g of typical polybenzoxazine (171°C). Furthermore, a series of linear aliphatic diamine-based benzoxazine monomers also have been studied by solventless synthesis. The kinetic rate of polybenzoxazine which investigate by spectroscopy was inversely

proportional to the aliphatic diamine chain length implying that polybenzoxazine from ethylenediamine (P-ad2) had the highest kinetic rate while polybenzoxazine from 1,12-Diaminododecane (P-ad12) showed the lowest kinetic rate. Additionally, the melting point also decreased with a function of diamine chain length (Allen *et al.*, 2007).

Moreover, increasing the crosslinking density of the polybenzoxazine network is expected to enhance both the thermal and mechanical performance. The addition of another reactive comonomer through the phenolic group is a common approach. (Ishida *et al.*, 2005, Kimura *et al.* 1999, and Agag *et al.* 2001). 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, nitrile (Kim *et al.*, 1999), propargyl (Agag and Takeichi, 2001), and allyl groups have been reported. These monomers yielding high-performance polybenzoxazines with much higher glass transition temperature (T_g) and improved decomposition temperatures in comparison with typical polybenzoxazines. In addition, using AB-type aminophenols instead of amines and phenols separately also enhance crosslinking density of the polybenzoxazine (Agag *et al.*, 2006). These material showed excellent thermomechanical properties as well as high thermal stability. Polymer alloys of polybenzoxazine with high performance polymers or with elastomers (Ishida *et al.*, 1996), hybridization with inorganic materials (Agag *et al.*, 2001) and metal oxide nanoparticles (Agag *et al.*, 2004) were also studied to obtain polybenzoxazine with improved properties.

2.2. Pervaporation Separation

Several techniques have been used for the removal of volatile organic compounds such as gas stripping, carbon adsorption, liquid-liquid extraction, and perstraction. However, these methods have some limitations including feed condition, large volume of by-product or high cost of post-treatments, etc. On the other hand, distillation is well-known technique for liquid separation but this

technology is not suitable for separation of close boiling, azeotropic or isomeric mixture.

Pervaporation is the partial vaporation of liquid through a dense polymeric membrane where the permeate undergoes a liquid-vapor phase change.

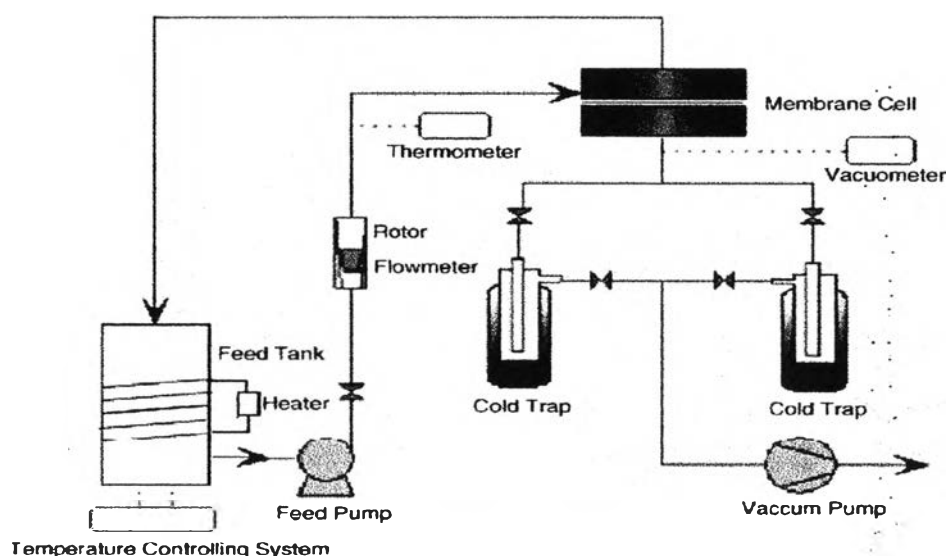


Figure 2.4 Scheme of the pervaporation apparatus (Chen *et al.*, 2009).

This technique can be operated in a single-pass mode. Unlike, for distillation in which the whole feed stream needs to be evaporated under reflux to get multiple phase changes in order to the vapor-liquid equilibrium. Therefore, pervaporation requires less energy consumption. The applications of pervaporation can be classified into three categories : (I) dehydration of organic solvents, (II) removal of dilute organic compounds from aqueous solutions, and (III) organic-organic mixture separation. Nevertheless, for industrial application's pervaporation is grouped into only two categories : is dehydration of alcohol and other organic solvents using hydrophilic or charged polymeric membranes and the removal of small amounts of organic compounds from contaminated water using hydrophobic membranes.

2.2.1 Application of Pervaporation in Petrochemical industry

Binning and co-workers at American Oil were the first to have done systematic work on pervaporation in 1950s but the process was not commercialized and remained a mild academic curiosity until 1982. When GFT (Gesellschaft für Trenntechnik GmbH, Germany) installed the first commercial pervaporation plant to separate water from concentrated alcohol solutions. In this plant, polyvinyl alcohol which is far more permeable to water than alcohol was used as composite membranes (fig 2.5.). The application in industries of pervaporation is the combining of distillation and pervaporation to produce dry alcohol.

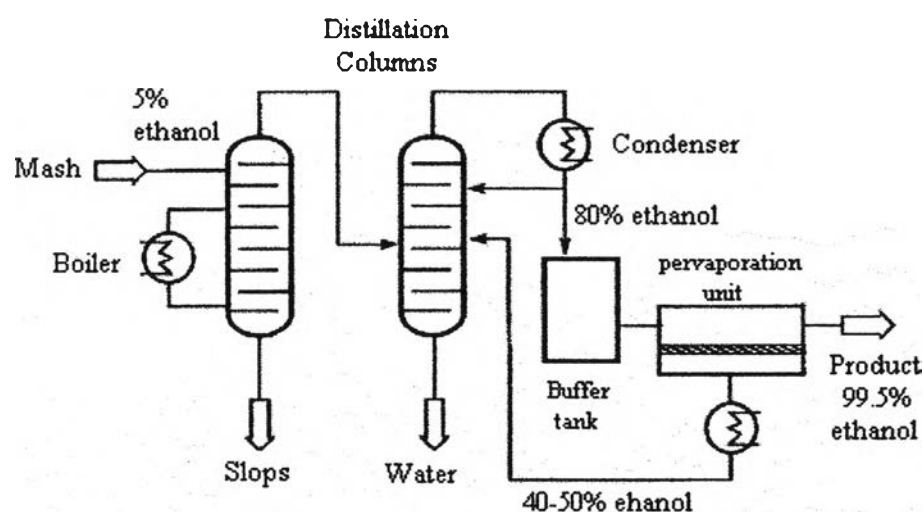


Figure 2.5 Flow scheme of a GFT plant for ethanol recovery (Baker, 2000).

The ethanol feed to the membrane generally contains ~10% water. The pervaporation process removes the water as the permeate, producing pure ethanol with less than 1% water and avoiding all the problems of azeotropic distillation. A great deal of effort is being made to apply pervaporation to other difficult separations. Another commercial pervaporation application is the separation of dissolved VOCs (volatile organic compound) from water, developed by Membrane Technology and Research, Inc. Relatively hydrophobic composite membranes, such as silicone rubber coated on a micro porous polyimide support membrane, were used

to obtain high separation factors for more hydrophobic VOCs such as toluene, benzene, chlorinated solvent, ester and ethers. Another commercial pervaporation processes is the separation of organics and water which is relatively easy due to organic solvents and water have very different polarity and exhibit distinct membrane permeation properties. In 1988, Separex reported the separation of methanol from methyl t-butyl ether/isobutene mixtures by setting up the first pilot-plant for an organic-organic application. This application achieved a good separation for cellulose acetate membranes (Spillman, 1995, Baker, 2004).

More recently, Exxon started a pervaporation pilot plant for the separation of aromatic/aliphatic mixtures by using polyimide/polyurethane block co-polymer membranes but this separation still has major separation problems in refineries (Baker, 2000, Mulder, 1996).

2.2.2. Polymer Membrane Researches for Pervaporation

For pervaporation process, water/alcohol separation is a well-known example in chemical industry in order to obtain liquid used as fuel from biomass sources (Xu *et al.*, 2003). Toraj *et al.* (2005) studied the pervaporation of methanol/water in comparison with ethanol/water mixtures by using PDMS membranes. They found that the total permeation flux of ethanol/water mixture was slightly higher than that of methanol/water mixture which caused by the different in molecular sizes.

Dense flat membranes are generally used for pervaporation. Satyanarayana *et al.* (2004) studied membranes for toluene-water separation by using two type of membranes: a dense membranes and asymmetric membrane of a thin layer polymer on a porous material. A dense membranes showed overall higher flux than that of a porous membrane which could caused by the molecular sieving properties of zeolite or the capillary condensation of the organic components.

To improve separation performance, many factors have to be considered depending on type of membranes. Degree of crosslinking is one of the factor that effect the separation efficiency. Quaternized poly(vinyl alcohol) (q-PVA) for ethanol dehydration can be crosslinked by glutaraldehyde. The crosslinking caused a

decrease in swelling but increased in water permeability of the q-PVA membranes (Zhang *et al.*, 2009). Qunhui and coworker (1995) studied dense and porous crosslinked chitosan (Cs) membranes for ethanol-water separation. They found that these membranes were selective to water. Moreover, this research also studied the temperature and membrane thickness which is one of many factors used to study in many researches to consider state of hold molecules because during solution process, the interaction among the permeates effected on enhancing of solution energy. Therefore, the increasing of temperature can reduced interaction of those permeates and restored interaction between the permeate and membranes. Moreover, the membrane thickness and mixture content also popular factors used to study their effect to the separation efficiency which this research reported that the suitable thickness should be thinner (Qunhui *et al.*, 1995). In case of the concentration polyphosphazene membranes was used as the example that it could be provided high separation efficiency in ethanol-water mixture with low ethanol content (Huang *et al.*, 2009).

Sulfonated polysulfone (PSf) with high degree of substitution provided high separation performance, increasing of permeation rate and separation factor because the hydrophilicity of sulfonyl group created water channels for dehydration (Chen *et al.*, 2001). For lithiated polysulfone membrane, the separation factor increased with increasing the degree of lithiation due to it improved high sorption selectivity (Chen *et al.*, 2001).

2.2.3 Measurement of Membrane Separation Efficiency

Partially cured polybenzoxazine (PBZ) was developed to use for pervaporation of water/ethanol mixture. Several parameters including feed concentration, temperature, and thickness, were varied. It was found that the transportation mechanism based on sorption and diffusion properties. Therefore, to measuring the separation efficiency of membrane, the important factors have to be evaluated following the reports of Feng *et al.*, (1997) that in developing membranes, three issues must be inquired including membrane stability, membrane productivity

and membrane selectivity. Generally, membrane productivity and membrane selectivity are used to determine.

Membrane stability is the ability of a membrane to maintain both the permeability and selectivity under specific system conditions for a range of time. Membrane stability is effected by the chemical, mechanical and thermal properties of the membrane.

Membrane productivity , frequently charaterized by permeation flux (J), is a measure of the quantity of a component that permeates through a specific area of membrane surface in a given unit of time. However, permeation flux depends upon both the intrinsic permeability and the effective thickness of a membrane. The permeation flux can defined as

$$J = M/At \quad (1)$$

where

M = permeate weight (kg)

A = effective membrane surface area (m^2)

t = pervaporation time (hr)

Furthermore, membrane selectivity for the separation of a mixture can determined by the separation factor from this equation

$$\alpha_{\text{water/ethanol}} = (Y_A/Y_B)/(X_A/X_B) \quad (2)$$

where

Y_A = the weight fraction of component A in the permeate

Y_B = the weight fraction of component B in the permeate

X_A = the weight fraction of component A in the feed

X_B = the weight fraction of component B in the feed

2.3 Bioethanal (Gasohol)

Biomass is one of the renewable energy resources, which exists in different forms. One of these clean forms of renewable energy is biofuel includes biodiesel,

bioethanol, biomethanol, biobutanol, biogas, etc. These fuels are produced from agricultural and industrial waste with a very low prime cost.

Biologically produced alcohols are called "Bioalcohols" which commonly are ethanol, and less propanol and butanol. These alcohols are produced by microorganisms and enzymes through the fermentation of many kinds of plants such as sugar cane, corn and tapioca, etc. Ethanol fuel is the common biofuel used worldwide which to replace gasoline. "Gasohol", which is a blending of bioethanol and gasoline at low concentration, does not require any change in the engine design. Moreover, using gasohol in the engine can improve the engine performance and exhaust emissions (Yucesu *et al.*, 2006; Hsieh *et al.*, 2002; Al-Farayedhi *et al.*, 2004). The another advantage of gasohol is it has higher octane number which effect from ethanol in gasohol can increase oxygen and then the machine can burn more slowly and completely. As a result, it can decrease the amount of hazardous substances such as hydrocarbon and carbon monoxide which cause to the greenhouse effect. Hence, it can use instead MTBE (Methyl Tertiary Butyl Ether) which was popular to add oxygen to benzene in the past. Most existing automobile petrol engines can run on blends of up to 15% of bioethanol with gasoline. However, ethanol-based gasohol with higher concentration of ethanol can damage rubber seals and diaphragms (Thiago *et al.*, 2007).