CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Bioethanol (Gasohol)

Biomass is one of the renewable energy resources, which exists in different forms. One of them is called biofuel, including biodiesel, bioethanol, biogas, etc. These fuels are produced from agricultural and industrial wastes with a very low prime cost (Ameri, Ghobadian et al. 2008).

Bioethanol is an environmentally friendly fuel, which has many attractive properties, such as clear colorless liquid, low toxicity, high octane substance, low production cost, low greenhouse gas and CO_2 emission, etc. Bioethanol is an alcohol produced by biological fermentation of carbohydrates derived from plant materials. In the fermentation process, yeast using monosaccharides as a food source was used to convert to ethanol via glycosis. Feedstocks for its production vary from chiefly cassava, sugarcane, and molasses, depending largely on local availability (Mogg 2004).

Gasohol (mixture of gasoline and ethanol) has higher octane number or antiknock property than gasoline, burns slower and more complete, resulting in reduced emissions of some pollutants (Paixão, Cardoso et al. 2007).There are many types of gasohol, depending on percentage of ethanol mixed with gasoline.

2.1.1 Types of gasohol

2.1.1.1 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 2-3 octane number higher than regular gasoline.

2.1.1.2 E15

E15 is a fuel mixture of 15% ethanol and 85% gasoline that is the highest ratio of ethanol to gasoline that is possible to be used in vehicles.

2.1.1.3   E20 and E25

E20 is a fuel mixture of 20% ethanol and 80% gasoline while E25 is a fuel mixture of 25% ethanol and 75% gasoline. These blends have been widely used in Brazil. E25 results in 2.65%CO and 12.14% CO_2 emissions.

2.1.1.4   E70 and E75

E70 is a fuel mixture of 70% ethanol and 30% gasoline while E75 is a fuel mixture of 75% ethanol and 25% gasoline. These blends are the winter blends that have been used in the United States and Sweden. The seasonal reduction of the ethanol content to a winter blend is to avoid cold starting problem at low temperature. E75 results in 1.24%CO and 10.25% CO_2 emissions.

2.1.1.5   E85

E85 is a fuel mixture of 85% ethanol and 15% gasoline that is generally the highest ethanol fuel mixture. This mixture has an octane number of about 105, which is lower than pure ethanol but higher than normal gasoline having an octane number of about 87.

2.1.1.6   E95

E95 for high compression engines is a fuel mixture of 95% ethanol and 5% gasoline. It is sometimes referred to as 'bus fuel' as it is usually used for diesel-powered engines. Because of the high ignition temperature of pure ethanol, the addition of ignition improver is necessary for successful diesel engine operation.

2.1.1.7   E100

E100 is pure ethanol fuel being used in Brazil. It is not currently compatible with vehicles manufactured for the U.S. market. Manufacturer approval of ethanol blends is found in vehicle owners' manuals under references to refueling or gasoline. The ethanol used in Brazil is the azeotrope and contain 4% of water. E100 has 0.73% CO and 9.51% CO_2 emission.

2.2 Benzoxazine

As mentioned in Chapter I, PBZ possesses various good properties and is prepared from a phenolic compound, a primary amine, and an aldehyde. These inexpensive raw materials are used to form benzoxazine monomers which are

polymerized by a ring-opening addition reaction, yielding no reaction by-product (Ishida and Allen 1996, Ishida 2011). The simply ring-opening polymerization reaction is shown in Scheme 2.1.
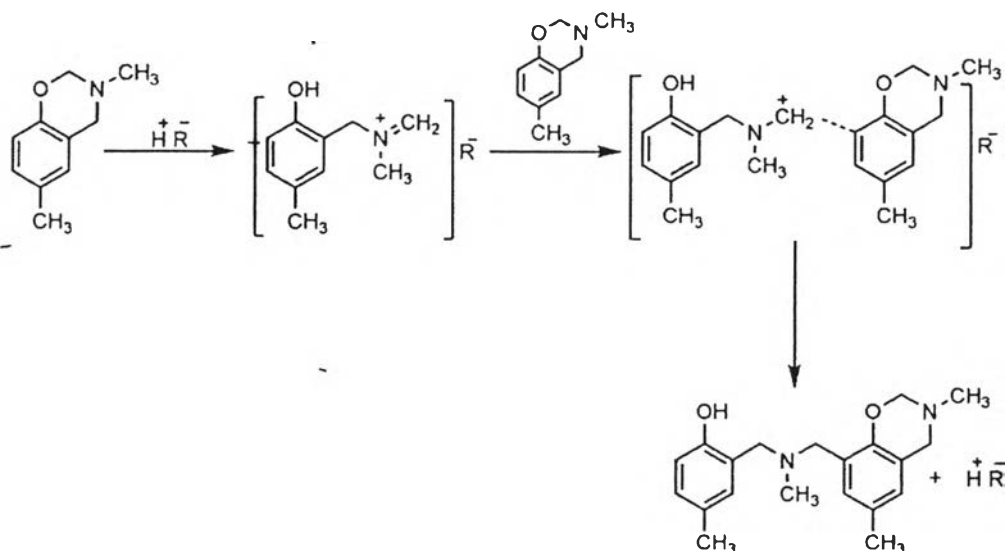

Scheme 2.1 Acid catalyzed ring opening polymerization of 3,4-dihydro-2H-1,3 benzoxazine (Dunkers and Ishida 1999).

Benzoxazine monomers are often synthesized using solvent or non-solvent methods. The different substitution groups of amines and phenols have been used to synthesize many types of benzoxazine monomer (Ghosh et al. 2007). Benzoxazine monomer can generally be categorized into three types, as follows;

2.2.1 Mono-Functional Group Benzoxazine Monomers

Mono-functional benzoxazines typically result in a linear or branched structure with a low molecular weight on the order of 500-2000 Da (Brunovska and Ishida 1999). Thus, mono-functional benzoxazine monomers show limited usefulness as structural materials. However, they might be useful as reactive diluents to facilitate the processing (Liu et al. 2011). The condensation reaction using primary amines with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers was first reported by Holly and coworker (1944). According to the informed process, 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. The synthetic procedure of the Mannich condensation for the benzoxazine synthesis was found by Burke and colleague (1965). It was produced in a solvent by first addition of amine to formaldehyde at lower temperatures to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and the ortho position of the phenol at the elevated temperature to form the oxazine ring as in Scheme 2.2.
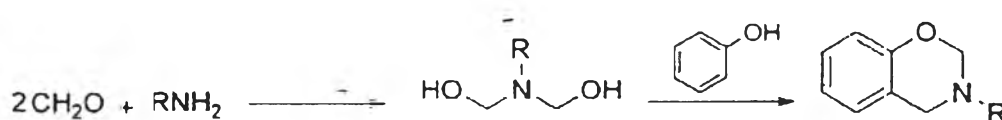

Scheme 2.2 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines (Burke 1949).

Burke and colleague (1964) found that a strongly basic amine with a less acidic phenol was more stable in the hot alcohols. The stability of the benzoxazine ring depends on the substituent. Another aminoalkylation reaction was resulted from the residence of more than one reactive ortho position in the initial product, as found by McDonagh and colleague (1968). Phenol having an ortho substituent gives a higher yield of benzoxazine. The synthesis with large amount of solvent results ina slow reaction rate.In some cases, the principle disadvantage which is the poor solubility of the precursors also participated with this process. Moreover, an increasing cost of the products and environmental problems are from the use of an organic solvent. The problems during processing of the benzoxazine resins are also resulted from the solvent residue in the precursors. Ishida and coworker (1996) thus developed a solventless synthesis in the melt state to defeat these defects. Agag (1995) reported the reaction mechanism and kinetic of this solventless synthesis for using these precursors to prepare an immense quantity of the benzoxazine monomer.

2.2.2 Di- Functional and Multifunctional Group Benzoxazine Monomers

Thermally accelerated ring-opening polymerization of bifunctional benzoxazine monomers and their properties were first reported by Ning and coworker (1994). The benzoxazines were cured with mono-functional group and phenol, resulting in low average molecular weight due to the formation-of only

oligomeric structures. In addition, the thermal dissociation of the monomer also occurred; no high molecular weight material could thus be made from this method. PBZ can enhance different performances in a wide range by using bifunctional benzoxazines to especially provide greater flexibility in molecular design than monofunctional monomers. Bifunctional benzoxazine monomers can be classified into two types. The first type is bisphenol-based bifunctional benzoxazine monomer which is produced by the reaction of bisphenol with either aliphatic or aromatic monofunctional primary amine. The other type is diamine-based bifunctional benzoxazine monomers, which can be obtained by using aromatic- or aliphatic diamines with a monofunctional phenolic structure of ortho-vacant position. These two bifunctional benzoxazine monomer types were reported by Ghosh and colleague in 2007. The bifunctional benzoxazine monomers reaction is shown in Scheme 2.3.
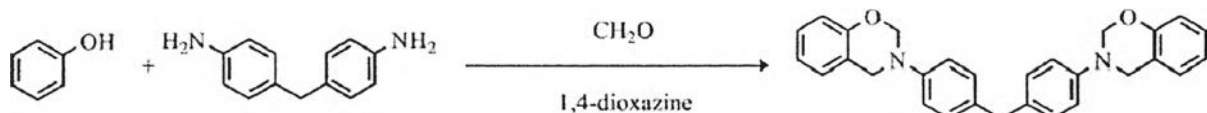
Scheme 2.3 Synthesis of DDM-based benzoxazine monomer (Ghosh et al. 2007).

### 2.2.3 High Molecular Weight Benzoxazine Precursors

Takeichi and colleagues (2005) synthesized high molecular weight PBZ precursors from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde. Some of the ring-opened structure was studied while the ratio of the ring-closed benzoxazine structure was high. These crosslinked PBZs were achieved during the film processing. The structures of a typical benzoxazine monomer and PBZ prepared from bisphenol-A, aniline, and formaldehyde are shown in Scheme 2.4.
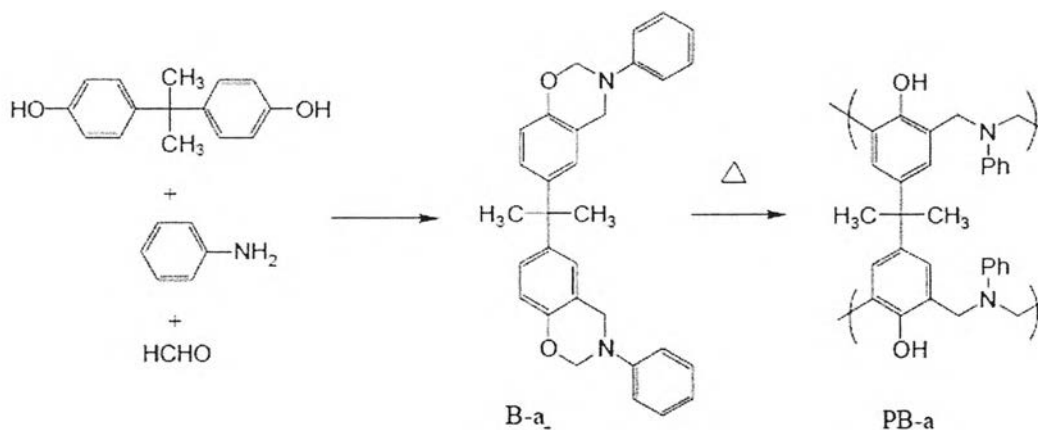
Scheme 2.4 A typical benzoxazine monomer prepared from bisphenol-A, aniline and formaldehyde (Takeichi et al. 2005).

In 2010, they also reported the synthesis of high-molecular-weight PBZ prepolymers by using α,ω-bis(aminopropyl)polydimethylsiloxane and bisphenol-A with formaldehyde. These PBZ prepolymers were achieved in free standing films by casting. They had shown good mechanical and thermal properties.

Agag and coworker (2007) studied novel high-molecular-weight PBZfrom AB-type benzoxazine precursors, derived from tyramine, *p*-aminophenols, and formaldehyde. The products showed excellent thermomechanical properties as well as high thermal stability when increasing the crosslinking density. The example of the cured PBZis shown in Scheme 2.5.
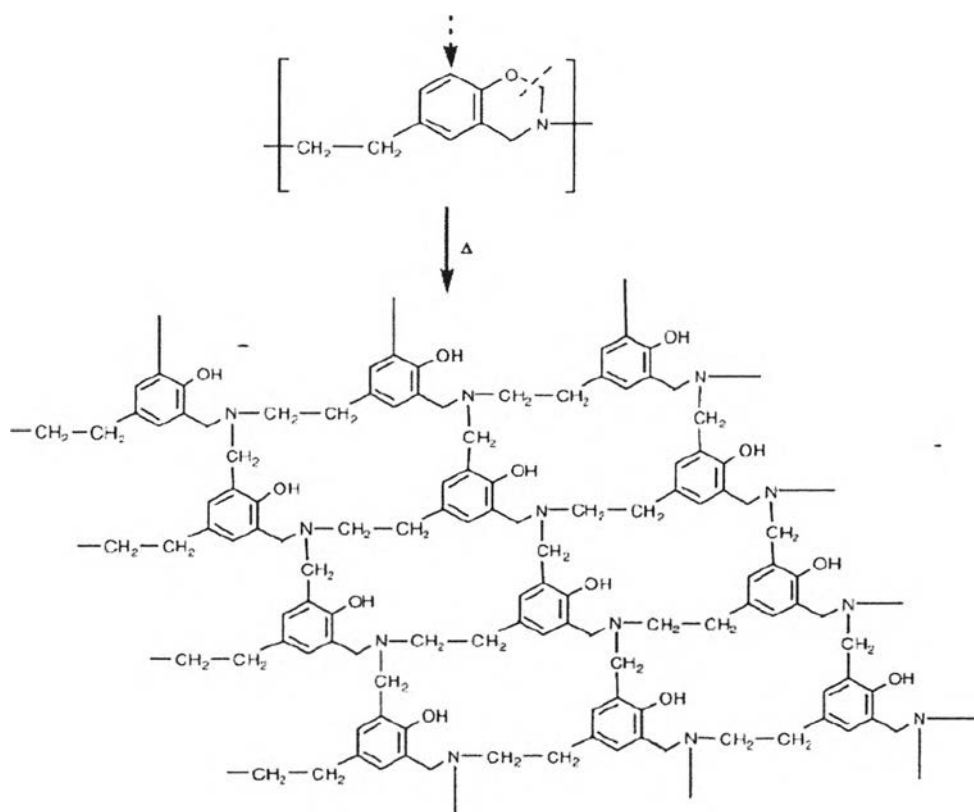
Scheme 2.5 The network structure of the cured PBZ obtained from the thermal cure of the AB-type benzoxazine precursors (Agag and Takeichi 2007).

2.3 Membrane Pervaporation

Pervaporation is a relatively new membrane separation process that has elements in common with reverse osmosis and membrane gas separation. In pervaporation, the liquid mixture to be separated (feed) is placed in contact with one side of the membrane and the permeated product (permeate) is removed as a low-pressure vapor from the other side (Scheme 2.6). The permeate vapor can be condensed and collected or released as desired. The chemical potential gradient across the membrane is the driving force for the mass transport.

The driving force can be created by applying either a vacuum pump or an inert purge (normally air or steam) on the permeate side to maintain the permeate vapor pressure lower than the partial pressure of the feed liquid. Pervaporation is

commonly considered to be a profitable complement to distillation for the separation of azeotropic and close-boiling mixtures, which requires at present the use of energy-intensive processes.

(a)

FEED — liquid — RETENTATE — VACUUM

vapour — CONDENSER

(b)

FEED — liquid — RETENTATE

vapour — CONDENSER
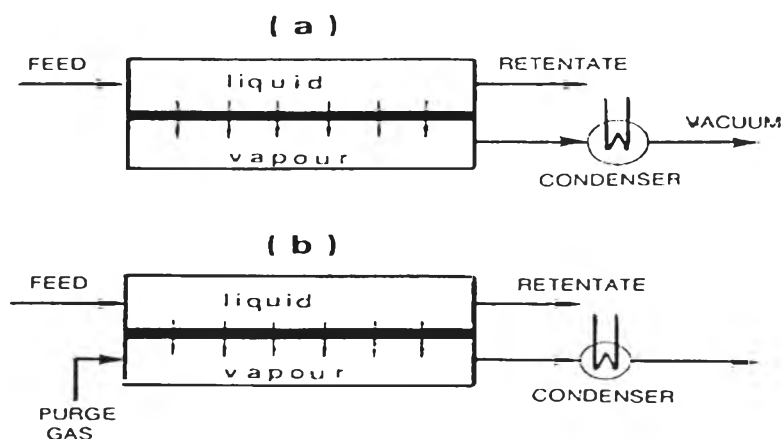
PURGE GAS

Scheme 2.6 Schematic diagram of the pervaporation process; (a) vacuum and (b) purge gas pervaporations.

2.3.1 Requirements for Membranes

Pervaporation is a rate-controlled separation process. In developing pervaporation membranes, three issues must be addressed:

2.3.1.1 Membrane productivity is a measure of the quantity of a component that permeates through a specific area of membrane surface in a given unit of time. Membrane productivity is frequently characterized by permeation flux, *J,* which relates the product rate to the membrane area required to achieve the separation. Note that permeation flux depends on both the intrinsic permeability and the effective thickness of a membrane.

2.3.1.2 Membrane selectivity is the performance of a given membrane in pervaporation, estimated in terms of its selectivity and the permeate flux. The assessment is based on the mass transfer of the preferentially permeating species, regardless of whether the permeate or the retentate is the target product of the pervaporation process. The selectivity of a given membrane can be estimated by using the following two dimensionless parameters:

- separation factor ($\alpha_{water-ethanol}$)

$$\alpha_{water-ethanol} = (\ Y_{water}/\ Y_{ethanol})\ /\ (\ X_{water}/\ X_{ethanol}) \qquad\qquad (2.1)$$

where:

Y_{water} = the mole fraction of water in the permeate

$Y_{ethanol}$ = the mole fraction of ethanol in the permeate

X_{water} = the mole fraction of water in the feed

- $X_{ethanol}$ = the mole fraction of ethanol in the feed

with $\qquad X_{water} + X_{ethanol} = 1$ and $Y_{water} + Y_{ethanol} = 1$

2.3.1.3 Membrane stability is the ability of a membrane to maintain both the permeability and selectivity under specific system conditions for an extended period of time. Membrane stability is affected by the chemical, mechanical, and thermal properties of the membrane.

2.3.2 Mass Transport in Membranes

There are principally two approaches to describe mass transport in pervaporation:

2.3.2.1 Solution-diffusion model

The mass transport by the solution-diffusion mechanism consists of three consecutive steps: (i) sorption of the permeant from the feed liquid to the membrane, (ii) diffusion of the permeant in the membrane, and (iii) desorption of the permeantas the vapor on the downstream side of the membrane (see Scheme 2.7).

2.3.2.2 Pore flow model

The mass transport by the pore flow mechanism also consists of three steps: (i) liquid transport from the pore inlet to a liquid-vapor phase boundary, (ii) evaporation at the phase boundary, and (iii) vapor transport from the boundary to the pore outlet (see Figure 2.2). The distinguishing feature of the pore flow model is that it assumes a liquid-vapor phase boundary inside the membrane, and pervaporation is considered to be a combination of the liquid and the vapor transports in series.
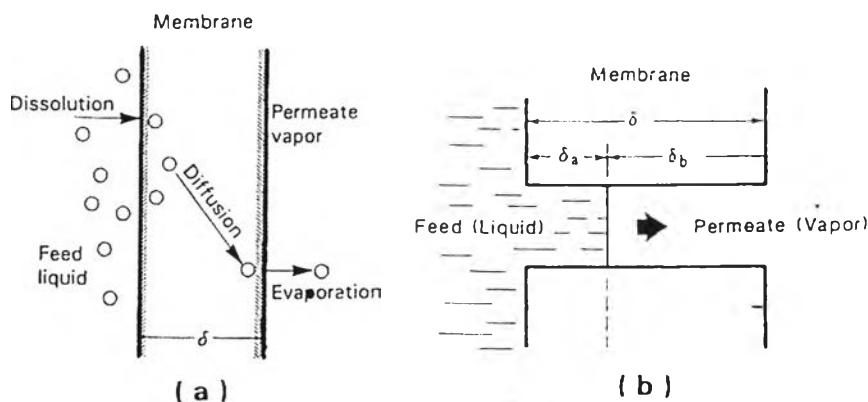
Scheme 2.7 Schematic representation of the pervaporation transport mechanism; (a) solution-diffusion and (b) pore flow models.

2.4 Pervaporation of Ethanol-water

Energy efficient dehydration of low water content ethanol is a challenge for the sustainable production of fuel-grade ethanol. Vasudevan and coworkers synthesized a pervaporative membrane by using a recently developed hydrophilic polymer membrane formulation, consisting of a cross-linked mixture of poly(allylaminehydrochloride)(PAAHCl) and a blend of 99 and 88% hydrolyzed poly(vinyl alcohol) (PVA). These polymeric membranes possess high water permeabilities at low feed water concentrations (<5 wt%) in ethanol compared to similar membranes in which all of the PVA portion was 99% hydrolyzed. A water-selective membrane system consisting of PAAHCl and blended PVA (99 and 88% hydrolyzed) has been developed for the dehydration of low water content ethanol. Blending of PVA88 with PVA99 imparted better permeability characteristics even at low water concentrations. The performance characteristics are tunable through blend composition and cure conditions. The polymer system described herein allows for two independent formulation variables: the ratio of PAAHCl–PVA and the ratio of PVA99–PVA88. Cross-linker concentration and cure conditions represent additional variables which can be enlisted to adjust final membrane performance characteristics. The membrane preparation procedure is straightforward, utilizes commercially

available materials, and could be a replacement for commercial PVA-based membranes. A prepared standalone membrane showed excellent stability over a 75-day period of continuous operation over a water concentration range of 0.5–42 wt%. Although a single PAAHCl–PVA membrane formulation capable of operating over a wide concentration range can be identified, it may be more advantageous to utilize membranes with different formulations at different stages of the solvent dehydration process to optimize performance, particularly in once-through continuous flow systems (Namboodiri and Vane 2007).

Pakkethati and coworker synthesized PBZ membranes from bisphenol-A, formaldehyde, and three different types of diamines: hda, tepa, and teta, via a facile "quasi-solventless" method. They employed those membranes to separate water from ethanol in a pervaporation system, to study the sorption and swelling behaviors. They found that when hda was used as a reactant, the resulting PBZ membranes showed the best service time and interestingly only water permeated through the membranes under the studied operation conditions. The total permeation flux was found to be 1.52 kg/m^{2}h and the separation factor was higher than 10,000. Additionally, an increased permeation flux was achieved by raising the temperature of the feed solution and decreasing the membrane thickness. The optimum conditions for this study were 70 °C for the feed mixtures using a 200 μm membrane thickness (Pakkethati et al., 2011).

2.5 Modified PBZ membrane for Ethanol/water separation

In the development of high-flux membranes, much effort has been made to introduce asymmetricity into the membrane structure in order to reduce the effective thickness of the membrane. These membranes generally have a thin dense skin layer supported on a microporous substrate, and thus, the permeation flux is substantially enhanced. All industrially important membranes are structurally asymmetric. An asymmetric membrane can be formed in an integral form or in a composite form. The difference between the two types of asymmetric membranes mainly lies in whether the skin and the substrate are made from the same polymer material. A composite membrane consists of a skin layer and a substrate that are made separately and from

two different materials. In practice, integrally skinned asymmetric membranes are often simply called asymmetric membranes.

2.5.1 Composite Membranes

Two major steps are involved in the preparation of composite membranes: casting of the microporous support first, followed by deposition of the selective dense layer (barrier) on the surface of the microporous support. One of the advantages of using the composite approach is that different polymers may be used as the barrier layer and the porous support, which allows a combination of properties that may not be available in a single material. Several methods have been developed to prepare composite membranes (Heinzelmann, 1991), including (i) casting of the barrier layer and membrane support separately, followed by lamination, (ii) direct coating of a polymer solution onto a support, followed by an appropriate post-treatment, and (iii) in situ formation of the barrier layer on a microporous support film.

Deng et al. reported that when a water-selective asymmetric polyamide membrane was laminated with PDMS, the membrane became more selective to water permeation. Their explanation to this phenomenon was that placing a PDMS membrane on top of the polyamide membrane prevented swelling of the polyamide membrane by the feed liquid, making the latter membrane contribute more effectively to selectivity (Deng et al. 1994).

Heintz and Stephan (1994) proposed a generalized solution-diffusion model for pervaporation through composite membranes by taking into account concentration polarization, coupled diffusion through the dense active layer, and the influence of the porous support layer.

2.5.2 Asymmetric Membranes

Asymmetric membranes are typically prepared from a single polymer solution via the phase inversion process. In this process, a homogeneous polymer solution is transformed into a two-phase system in which a polymer-rich solid phase forms the rigid membrane structure, while a polymer-poor liquid phase forms the voids. To prepare this kind of membrane, the polymer should be dissolved in a suitable solvent. The homogeneous solution is formed into a film in such a way that the desired shape (e.g., flat, tubular, or hollow fiber) is obtained. The polymer

solution is treated in a specific way to precipitate the polymer, followed by a suitable drying process.

Tsai and coworker synthesized chitosan/polyacrylonitrile (PAN) composite hollow fiber membrane to investigate the pervaporation performance of aqueous alcohol solution. The chitosan layer of composite hollow fiber membrane was formed by dip-coating chitosan solution onto the outer surface of NaOH-hydrolyzed PAN hollow fiber membrane. γ-Glycidoxypropyltrimethoxysilane (GPTMS) was used as the cross-linking agent of chitosan. The structure and the morphology of the hydrolyzed PAN hollow fiber membrane were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electronic microscopy (SEM) and atomic force microscopy (AFM). The pervaporation performances of aqueous alcohol solution through the hydrolyzed PAN hollow fiber membrane and the chitosan/PAN composite hollow fiber membrane were investigated. The performance was found to be 145 g/m^2 h permeation rate with 99.7 wt% water content in permeate when using 90 wt.% aqueous *iso-propanol* (IPA) solution at 25 °C through chitosan (1.5 wt.%)–GPTMS (2 wt%)/PAN composite hollow fiber membrane. Furthermore, the long-term pervaporation stability for chitosan/PAN composite hollow fiber membrane was also investigated. The pervaporation efficiency of 70wt.% aqueous IPA solution at 25 °C could be maintained after 330 days of operation for the chitosan–GPTMS/PAN composite hollow fiber membrane while the GPTMS-free chitosan/PAN composite hollow fiber membrane was lost its pervaporation efficiency after 8 days of operation (Tsai et al. 2008).